AD-A174 025

ARCTIC HAZE: NATURAL OR POLLUTION?

A Progress Report and Renewal Proposal to the

Office of Naval Research
Arctic Program
800 N. Quincy St.
Arlington, VA 22217

1 November 1986

Principal Investigator Dr. Kenneth A. Rahn, Research Professor
Co-Principal Investigator Dr. Douglas H. Lowenthal, Marine Scientist
Center for Atmospheric Chemistry Studies
Graduate School of Oceanography
University of Rhode Island
Narragansett, Rhode Island 02882-1197

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PROPOSAL

TITLE: ARCTIC HAZE: NATURAL OR POLLUTION?

DATE: 1 November 1986

AGENCY: Office of Naval Research - Arctic Program

Submitted by
THE UNIVERSITY OF RHODE ISLAND

Total Amount Requested: $431,830

Proposed Starting Date: 1 January 1987

Duration of Program: 33 months

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STATEMENT OF SUBMISSION

The following progress report and renewal proposal, "Arctic Haze: Natural or Pollution?", is hereby submitted to the Office of Naval Research, Arctic Program, for consideration as an extension of Contract N00014-84-C-0035, of the same title. This proposal is not being submitted to any other agency for financial support, although certain costs are to be shared with other grants and contracts awarded to the University of Rhode Island.

ABSTRACT

    A three-year program of continued research on Arctic haze is planned. The
research builds on the accomplishments of the past three years and extends them,
with particular emphasis on strengthening the new elemental tracer system,
attempting to determine the history of Arctic haze by analyzing the
Russian/Norwegian ice core from Nordauslandet, and analyzing aircraft samples
from the AGASP II aircraft experiment of spring 1986. The tracer system will be
improved in at least three ways: its statistical aspects will be refined, inno-
vative ways of deriving signatures from hard-to-sample areas will be explored,
and the tracer power of several noble metals will be determined.(by a new gra-
duate student who has work extensively with these elements in the past). >From
the Nordauslandet core, as many as 100-200 samples will be analyzed for trace
elements with our new technique developed under DOE sponsorship: we hope to use
the results to write both the modern history of Arctic haze and the history of
the various regions contributing to it. An extensive set of aircraft samples
from AGASP II will be analyzed for trace elements and compared with the results
of other investigators. In addition, we will assist Dr. B. Ottar of the
Norwegian Institute for Air Research in planning for the Fourth Symposium on
Arctic Air Chemistry, to be held in Oslo in September 1987.

TABLE OF CONTENTS

THESES

INTERNATIONAL COOPERATION

SYMPOSIA

MISCELLANEOUS

ii

I. PROGRESS REPORT: AUGUST 1983 - OCTOBER 1986

A. HIGHLIGHTS OF ACTIVITIES AND RESULTS

- Using an $89,140 grant from the ONR/DOD's University Research Instrumentation Program as a nucleus, an integrated word/data-processing system was established at URI, to strengthen our new computer-based neutron-activation system. New items included a large gamma detector, larger magnetic tape, 30-MB Winchester disk, supplemental control terminal, memory and processor boards for the computer, and a CPT word/data-processing system which was linked to the analytical system to produce a true fused data-acquisition/processing system.

- Major features of the new seven-element tracer system for pollution aerosol were formalized. Two major articles in SCIENCE in 1984 and 1985 described the technique and how it was used in eastern North America.

- We published two popular articles in NATURAL HISTORY on the tracer system, the first by K. Rahn on Arctic haze in 1984, and the second by K. Rahn and D. Lowenthal in 1986 on the use of the system in the Northeast.

- On 11 August 1986, NEWSWEEK devoted a page to our tracer system and its uses.

- The tracer system was patented on 5 August 1986.

- In March 1986, EPA formally approved the tracer system as a method for determining regional sources of pollution aerosol.

- We have begun to use atomic absorption to search systematically for additional elements for the tracer system. Of nine elements considered so far, only one has been eliminated from consideration.

- We have begun to use neutron activation with post-irradiation chemical separations to evaluate the tracer potential of 6-7 noble metals, via a new graduate student.

- We have begun to explore alternative ways of generating signatures for regions with difficult access, using aerosol samples collected in other ways and from deposition rather than aerosol. Initial results with deposition are encouraging, provided that samples are taken and interpreted carefully.

- Under a DOE grant, the tracer system has been successfully extended to precipitation. Of the seven elements used for aerosol, at least four work well in precipitation.

- Regional signatures were developed for the Central Soviet Union, the Western Soviet Union, Northeastern China, Southwestern China, and Manchuria.

1

- Sources of Arctic haze at Barrow during winter 1979-80 were quantified. The USSR contributed about 70% of the mass of the tracer elements and about 40-50% of the sulfate. Europe contributed most of the rest.

- A direct anthropogenic effect on pulses of CO_2 at Barrow was found by means of the aerosol tracer system.
- Sources of Arctic aerosol during AGASP I (spring 1983) were quantified with the tracer system. Major pulses in both the eastern and western Arctic came predominantly from the Soviet Union. Sources over the entire period were similar to those of winter 1979-80, but with 10-30% more from Europe.

- A summer haze event over Alaska during July 1986 was shown to be from European industry, with transport surprisingly similar to winter.

- Aerosol samples continued to be taken in Barrow, Iceland, and Rhode Island. European sampling generally ceased.

- We participated in the NOAA/ONR Arctic Gas and Aerosol Sampling Program of spring 1983 by sampling and analyzing filters from the aircraft and the ground. In addition, K. Rahn took part in the Norwegian leg, both as consulting meteorologist and aboard the aircraft.

- For AGASP II (1986), K. Rahn gave overview talks at the planning meetings and served as Chairman of the Tracer Committee, and D. Lowenthal analyzed filters from the aircraft flights.

- The M.S. thesis of Noëlle F. Lewis on particle-size distributions of trace elements in Arctic aerosol was completed in May 1985.

- The Ph.D. thesis of Douglas H. Lowenthal on operational and statistical aspects of the tracer system was completed successfully in May 1986.

- K. Rahn visited China in fall 1983, made contact with Mr. Zhao Dianwu of the Institute of Environmental Chemistry in Beijing, and eventually got a series of samples from the Beijing-Tianjin area which was used to derive a regional signature. In fall 1985, we received an additional series of samples from southwestern China which confirmed the results from northeastern China.

- In 1985 and 1986, Mr. Su Weihan and Mr. Zhao Dianwu, both of the Institute of Environmental Chemistry, Beijing, visited URI.

- In 1984, K. Rahn visited the Soviet Union for two weeks to begin to plan a joint experiment on trace elements in aerosols. Since then, the project has been delayed by the USSR, however.

- In 1984-85, we cooperated with Prof. S. Tsunogai of Hokkaido to collect and analyze six months of daily aerosol samples from Okushiri Island just west of Hokkaido, in search for aerosol from the Central Soviet Union there. The experiment seems to have succeeded - that aerosol and others were found in abundance.

- The Third Symposium on Arctic Air Chemistry was held at the Atmospheric Environment Service in Toronto 7-9 May 1984. It was hosted by L.A. Barrie of AES and chaired by K. Rahn. In total, 31 papers were presented. K. Rahn served as Guest Editor for the December 1985 issue of <u>Atmospheric Environment</u>, which was devoted to the Third Symposium.

- K. Rahn attended the International Symposium on Arctic Atmospheric Pollution at the Scott Polar Research Institute, Cambridge, England, 2-5 September 1985, and presented a paper written with D.H. Lowenthal. K. Rahn also served on the planning committee for the symposium.

- An episode of Sahara dust was discoved over Rhode Island in July 1984.

- Radioactivity from Chernobyl was measured in air, rain, grass, and milk of Rhode Island with the gamma-ray counting system described above. Aerosol samples from Barrow were also counted in near-real time, and used to determine that the plume hit the American West Coast before it reached Alaska.

- Ideas on the fate of Arctic haze were formulated, starting from diverse observations of the haze reaching midlatitudes in winter.

B. ACTIVITIES AND RESULTS

1. Integrated word/data-processing system established at URI by grant from ONR/DOD

On 15 April 1984 we were granted $89,140 under the second round of ONR/DOD's University Research Instrumentation Program to strengthen our new computer-based neutron-activation system. The nucleus of the system had been bought during late 1983 and early 1984, with funds mostly from EPA and supplemented by ONR, and consisted of a Nuclear Data Model 6700 processor, magnetic tape deck, 10-MB Winchester disk, three large gamma-ray detectors, and a printer. The ONR/DOD funds were used to purchase three major types of additional items: (1) a large (39%) gamma detector for counting small Arctic samples with high efficiency, (2) several electronic components (larger magnetic tape, 30-MB Winchester disk, supplemental control terminal, memory and processor boards for the computer, etc.), and (3) a CPT word/data-processing system to be linked to the analytical system. The result was a true fused data-acquisition/processing system which allows us to analyze aerosol samples more efficiently, and thus to develop the elemental tracer system and apply it to Arctic haze more rapidly and cost-effectively than otherwise possible.

The idea and the components have worked out very well. The integrated system does everything we had intended, and is the only one of its type that we know of. Our efficiencies have been increased significantly, and we are able to process the large numbers of samples that are so important to distinguishing between environmental signals and environmental noise, but which are often compromised when proper facilities are not available. The large detector has improved our counts of long-lived radionuclides markedly; the disk enables several investigators to store their individual series of spectra comfortably; the large magnetic tape allows us to archive all raw spectra on a conveniently small number of large tapes; the control terminal allows two investigators to examine different sets of spectra as they are being accumulated; the memory and processing boards allow the built-in computer to work on multiple programs faster and more flexibly; the link to the word/data processor allows us to transfer our large tables of elemental data from the computer to the word processor and print them out in an attractive format that can be read easily by people outside our group.

Because we have been able to process many more aerosol samples than formerly, our elemental tracer system has been solidified and tested thoroughly. We have been able to undertake larger experiments than in the past, such as the Okushiri Island study described below.

4

NEW ELEMENTAL TRACER SYSTEM FOR POLLUTION AEROSOL

2. <u>Formalization of the seven-element tracer system</u>

Our elemental tracer system began in 1980 with Mn and V. The use of only two elements was a temporary measure, and during late 1982 and early 1983 we investigated several other potential elements. By mid-1983 we had settled on seven elements, the system which has remained stable until now. The other five elements, As, Se, Sb, Zn, and In, were selected as having the best combination of the desirable properties: ease of analysis by neutron activation, pollution origin in the aerosol, and submicron particle size.

After the elements were selected, the other aspects of the tracer system had to be settled as well. They included:

- Expressing the elements as ratios to Se rather than as absolute concentrations.
- Establishing ways to generate regional signatures.
- Testing procedures for apportioning the elements among regional signatures.
- Testing the system for stability to random perturbations in samples and signatures.
- Learning how to deal with sulfate, most of which is formed from SO_2 during transport and so cannot be made a direct part of the tracer system.
- Checking to see whether the results of the tracer system made environmental sense, or could be verified against other techniques such as long-range transport modelling.

All these topics have now been resolved favorably. Much of this developmental work was part of Dr. Lowenthal's Ph.D. thesis, "Regional source apportionment and related statistical topics", University of Rhode Island, 1986.

3. <u>Two major articles in SCIENCE on the tracer technique and its applications</u>

In 1984 and 1985, we published two major articles in <u>Science</u>, the first of which described the seven-element regional tracer technique and the second of which detailed how it was used to determine sources and transport of pollution aerosol in eastern North America. The 1984 article is reproduced in the Appendix.

Although the topic of the second article was not a direct part of our ONR Contract, we used the extensive data sets for North America to refine and test various statistical and operational aspects of the tracer system. The results have benefited our Arctic Haze research as well, and were used in preparing the Lowenthal-Rahn article on sources of aerosol at Barrow, Alaska which appeared in the December 1985 Arctic issue of <u>Atmospheric Environment</u>. The existence of large trace-element data sets for North America, generated under the EPA and OEUI projects, has been a boon to this ONR project, for most of Dr. Lowenthal's

efforts during the last three years have had to go toward developing the technique itself rather than analyzing samples.

4. Two popular articles in NATURAL HISTORY on the tracer system

We believe that it is extremely important for the results of scientific projects to be disseminated to the lay public. Thus, we were pleased when Natural History magazine encouraged K. Rahn to write an article on Arctic haze in 1984, and we were even happier when they came back for another article in 1986, this time by Rahn and Lowenthal on transport to the Northeast. Natural History reaches an entirely different audience than our conventional publications do; each of these articles has generated large numbers of requests for reprints from all over the world. The first article described the tracer system and how it led to the Soviet Union as a major source of Arctic haze. The second article reviewed the tracer system briefly, then concentrated on sources of pollution aerosol for New England and how they depend on weather patterns.

5. Article in NEWSWEEK on the tracer system

In its issue of 11 August 1986, NEWSWEEK devoted nearly an entire page to our tracer system and how it is being used at URI to determine sources of pollution aerosol and acid rain in New England. In addition to citing results and their implications, the article noted the patent (Section 6 below) and the approval of the system by EPA (Section 7 below).

We are extremely pleased that NEWSWEEK chose to honor our work by writing so extensively about it. This feature is one of the most prominent pieces of publicity ever given to URI in the national media. It stimulated a flood of secondary and tertiary writeups in other national media, including the New York Times, Inside EPA, the Sierra Club newsletter, Coal and Synfuels Newsletter, etc. A sizeable story will appear in National Wildlife of February 1987.

6. Patent on the tracer system

Our regional elemental tracer system is unique. No other group has anything comparable. To recognize this, the University of Rhode Island encouraged us to patent the technique. When they first proposed this in 1984 we resisted, but after discussing it further, we decided to apply.

On 8 July 1986 the University was notified that U.S. Patent No. 4,603,575, "Elemental tracer system for determining the source areas of pollution aerosol", was to be granted to the Rhode Island Board of Governors for Higher Education on 5 August 1986, which it was. Without the continuous support of ONR, this tracer system would never have reached fruition. A copy of the patent is included in the Appendix.

6

7. EPA formally approves the tracer system and its results

As of March 1986, EPA has officially approved our regional tracer system and the information on sources and transport of pollution aerosol in eastern North America deduced from it. The vehicle for this approval is the Final Report of our EPA project entitled "Elemental tracers applied to transport of aerosol from Midwest to Northeast", which is available from NTIS as report EPA/600/3-86/015. EPA is also circulating a Project Summary widely, available under the number EPA/600/S3-86/015. The significance of this development to ONR is that "its" tracer system and results derived from it are now approved in full by the highest environmental agency in the land, without scientific disclaimer. This is a big step forward for us. It was not easy; EPA had doubts about the tracer system in the beginning, principally because no one there had studied it carefully enough. After a full year of peer and administrative review, however, EPA changed its mind and now supports the system.

8. Systematic search for additional elements for tracer system begun by atomic absorption

From the beginning, we have wanted to include as many elements in the tracer system as possible. The current seven were chosen because they were the best of the neutron-activation elements, i.e., the "easiest" because no change in analytical technique was needed.

But many other elements might also be suited for the tracer system. Their potential should be investigated before the system is considered complete. They can be surveyed systematically by checking to see how well they satisfy the same criteria used to select the original seven: they must be strongly pollution-derived in aerosol, have the bulk of their mass in the fine-particle (submicron) range, and be analyzable with precision and accuracy by an accepted technique.

The pollution-derived criterion can be checked from the aerosol-crust enrichments of the elements, because high enrichments of nonmarine elements mean that they are pollution-derived. Figure 1 shows a periodic table of enrichments (Rahn, 1976). Nearly all the pollution-derived elements are found in the lower right portion of the periodic table. From Figure 1, we have determined that 21 additional elements qualify as potential tracers, based on enrichments alone.

The second criterion, that the element must be fine-particle in the aerosol, usually follows from the first, that is, most enriched elements are also fine-particle. This criterion becomes important at a later state of the investigation.

The third criterion, having an available analytical technique, is addressed in Table 1. To choose the most appropriate additional analytical techniques for us, we adopted two criteria: (1) neutron activation should be used wherever possible, so that we can build on our strengths, and (2) other analytical techniques should be proven and available at the Graduate School of Oceanography. Two major techniques emerged from these criteria: the Nadkarni-Morrison method for determining noble metals by neutron activation coupled with post-irradiation

7

I																VII	0
H̲	II												III	IV	V	VI	H̲	He ND
Li	Be̲												B̲	C̲	N̲	O ND	F	Ne ND
Na	Mg												Al	Si	P	S̲	Cl̲	Ar ND
K	Ca	Sc	Ti	V̲	Cr̲	Mn̲	Fe̲	Co̲	Ni̲	Cu̲	Zn̲	Ga̲	Ge̲	As̲	Se̲	Br̲	Kr ND
Rb	Sr	Y	Zr	Nb	Mo̲	Tc ND	Ru*	Rh*̲	Pd*̲	Ag̲	Cd̲	In̲	Sn̲	Sb̲	Te̲	I̲	Xe ND
Cs̲	Ba̲	La-Lu	Hf	Ta	W̲	Re*̲	Os*̲	Ir*̲	Pt*̲	Au̲	Hg̲	Tl*̲	Pb̲	Bi̲	Po ND	At ND	Rn ND
Fr ND	Ra ND	Th, U															

Sc = Nonenriched; V̲ = Intermediate; Z̲n = Enriched
ND = No data; * = classification uncertain

Figure 1. Periodic table of aerosol-crust enrichments
(after Rahn, 1976).

8

Table 1. Potential additional tracer elements and
analytical techniques for measuring them

Element	Neutron activation with radiochemical separations	Atomic absorption spectrophotometry	Other	Unknown
F			Ion chrom./ spec.-ion electrode	
Ni	x			
Cu		x		
Ge				x
Mo		x		
Ru	x			
Rh				x
Pd	x			
Ag	x	x		
Cd	x	x		
Sn	x	x		
Te		x		
W	x			
Re				x
Os	x			
Ir	x			
Pt	x			
Au	x			
Tl		x		
Pb		x		
Bi		x		
21	11	9	1	3

chemical separations, and atomic absorption. Of the 21 candidate elements, only Ge, Rh, and Re seem not to be determinable by these techniques of slight extensions of them. Of course, merely having an analytical technique for an element does not guarantee that it can be measured well enough in the aerosol; listing the techniques is only a preliminary screening process.

After working exclusively with seven elements for the last three years, we have begun to systematically evaluate the other 21, using atomic absorption and neutron activation. Atomic absorption spectrophotometry has long been used at the Graduate School of Oceanography for determining several useful elements in aerosols. Its virtues are its great specificity and sensitivity, especially when graphite tubes are used to atomize the samples. Its disadvantages are the long times needed to prepare the samples and analyze them element by element. It is slow but guaranteed.

When only Pb and Cd are to be determined by atomic absorption, it is sufficient to leach them from the filter overnight in dilute nitric acid. They can then be measured on a flameless AA unit such as a Perkin-Elmer Model 603, using the method of standard additions. Although standard additions is time-consuming, we feel that it is the only way to guarantee that matrix effects, which can vary strongly from sample to sample for certain elements, are completely eliminated. Two years ago, a state-funded graduate research assistant used this procedure to determine for us that Pb and Cd are useful tracer elements.

When a larger suite of elements is to be determined by AA, the samples must be prepared more rigorously. A portion of the filter is first placed in a Teflon vial and dry-ashed in a low-temperature asher. The residue is then totally dissolved by being taken up in a mixture of concentrated nitric and hydrofluoric acids and allowed to stand at room temperature for at least two weeks. It is then diluted and analyzed, using the method of standard additions for elements with known matrix effects and the normal comparative method for elements free of matrix effects.

Earlier this summer, Mr. Andrew Hudson, a former graduate student here, offered to survey nine elements by the full AA procedure just described. We took him on, under this ONR Contract, because he offered extensive experience at very reasonable cost (he worked after-hours for us and did only what we needed). The elements were Pb, Cd, Mo, Ag, Sn, Tl, Te, Be, and Bi. To date he has looked for six of the nine elements (Pb, Cd, Mo, Ag, Sn, Tl) in approximately one-half the signature samples given to him, with the other samples and elements to be measured during the fall. Of the initial nine elements, only Be was found to be impractical analytically. At this point, we are cautiously optimistic that atomic absorption analysis will yield 5-7 elements with significant tracer power. If so, the resolving power of our tracer system will be increased markedly.

Of course, this venture is pure research. Once we learn which elements can be profitably added to the tracer system, they will have to be measured systematically on actual suites of aerosol samples in order that their potential as tracers be realized. The additional analytical time for atomic absorption, which will be considerable, for atomic absorption is not rapid, probably cannot be accommodated under the present ONR Contract.

10

9. Systematic evaluation of noble metals as potential tracers begun by new ONR graduate student D. Elroi

Among the 21 additional potential tracer elements are 6-7 noble metals (depending on how Ag is counted). For some time, we have wanted to investigate which of these elements are suitable for our tracer system. In the last month, an opportunity arose which we could not refuse: a new graduate student arrived who had extensive experience with the noble metals and who was eager to work with our group. Mr. David Elroi comes to us from Israel and England, and will pursue an M.S. thesis, under our ONR Arctic Haze Contract, on the tracer power of noble metals and related elements.

Mr. Elroi has already begun by surveying the literature on the loss to the atmosphere of noble metals from catalysts and other industrial processes, in an attempt to get a feeling for which elements might be most useful as tracers and what their major sources might be. He is well into this phase of his work. Next, he will determine how many noble metals can be measured in aerosol using neutron activation and post-irradiation chemical separations. To do this, he will adapt a published procedure for measuring Au, Pt, Ir, Pd, Ru, and Os in geological materials by neutron activation in conjunction with Srafion NMRR, an ion-exchange resin specific for noble metals (Nadkarni and Morrison, 1974). In the original procedure, a sample of powdered rock is irradiated, then fused and passed through a column containing the Srafion NMRR, which selectively retains the noble metals. The metals can then be eluted from the column and counted on Ge(Li) gamma-ray detectors or counted directly on the resin.

This technique should work as well for noble metals in aerosol as in rock. At the reactor of the Rhode Island Nuclear Science Center, we can easily expose samples to 2-5 times the dose of neutrons that Nadkarni and Morrison used. Our detectors are 5 times as efficient as theirs were. Per unit mass of crustal material in aerosol, the noble metals should be enriched by factors of 100-1000 relative to the crust (Rahn, 1976). Therefore, to get the same number of decays per sample that Nadkarni and Morrison did, we need only irradiate 1/1000 to 1/25,000 as much crustal mass. Nadkarni and Morrison irradiated 300-500 mg; we would need only 10-500 µg of crustal material. We easily satisfy this requirement: in the northeastern U.S. and the Arctic, respectively, we routinely irradiate 2000 and 200 µg of crustal material.

As necessary, Mr. Elroi will adapt the procedure to the needs of aerosols. Because the noble metals are probably not in the elemental state in aerosols, they should dissolve more easily after irradiation than the native elements in rock; it may be possible to eliminate the fusion step and simplify the procedure considerably. In adapting the procedure, Mr. Elroi will be aided by another member of our group, Dr. Roy Heaton, who has considerable experience with ion-exchange resins.

After developing the analytical procedure, Mr. Elroi will measure the noble metals in our various signature samples and determine which are suitable for the tracer system. He will conclude his thesis by applying his analytical techniques and signatures to one or more suites of aerosol samples from the Arctic,

to see how much the noble metals add to our ability to discriminate the sources of Arctic haze in actual practice.

Mr. Elroi's effort with noble metals will run parallel to Mr. Hudson's with atomic absorption. Together, they will investigate the tracer power of 15 additional elements, i.e., the majority of the remaining candidates. Thus, within 2-3 years, we should have a very good idea of the final list of elements in the system. If even one-half the additional elements work out, the tracer power of our system could be greatly magnified.

10. Alternative ways of generating signatures in difficult regions explored

We are frustrated by the difficulty of generating elemental signatures in certain regions. Regions close to home can be sampled with relative ease, but more distant regions often pose problems such as distance, logistics, lack of contact people, language barriers, electric power, or simply closed borders. If one or more innovative ways for generating regional signatures could be developed, the dividends could be very great.

Consequently, we have begun to explore alternative ways to generate regional signatures. Two general approaches can be imagined: from aerosol samples collected in other ways and from deposition rather than aerosol. We are trying both approaches: aerosol from automobile air filters and deposition from inert surfaces and plants.

Analyzing the air filter from an automobile engine seemed promising because the huge volumes of air pulled through these filters should make them easy to analyze, even if the filter material was impure. We tested a Toyota filter and confirmed that it could be analyzed, but ran into two problems: (1) the material on the filter was strongly crustal in composition, probably from resuspended road dust, and (2) the filter material itself was too heavily loaded with Sb. We plan to continue working with auto filters, by analyzing one from an American car.

Working with deposition is extremely attractive in principle, for large amounts of aerosol are continually being deposited from the atmosphere to surfaces and plants. Relatively little information is available on how closely the detailed elemental compositions of various types of deposition resemble the parent aerosol, however, so that we need to generate our own data before we can decide whether this approach is feasible. Fortunately, our DOE study of trace elements in 18 months of precipitation at Narragansett, RI (described in the next section), has given us one of the best data bases in existence. Thus we already know the composition of aerosol and wet deposition at Narragansett very accurately. By characterizing other measures of deposition at Narragansett, we can compare them with each other and with the parent aerosol and see which are satisfactory surrogates for which.

It must be kept in mind, however, that deposition is inherently more complex than aerosol, and may differ systematically from it. Factors contributing to differences between deposition and aerosol include:

12

(1) Multiple sources for deposition. Deposition is the sum of dry plus wet processes. Dry deposition has vapor-phase and particulate components, but for our tracer elements, the vapor-phase component is negligible. Dry deposition is continuous and derived from surface aerosol, whereas wet deposition (precipitation) is sporadic and derived more from aerosol aloft. For fine-particle elements such as comprise our tracer system, wet deposition is generally considered to be an order of magnitude more important than dry deposition, at least in moist regions. Thus to a first approximation, we may equate deposition with precipitation.

(2) Enrichment of coarse particles in deposition relative to aerosol. Both wet and dry deposition are enriched in coarse particles compared to the parent aerosol, by as much as an order of magnitude. Thus, deposition cannot be used to determine signatures which involve both coarse- and fine-particle elements. Deposition can provide satisfactory signatures for our tracer system, however, which uses fine-particle elements only. In fact, our DOE study of precipitation has shown that at least four of our seven tracer elements (As, Se, Sb, V) are not fractionated measureably in wet deposition relative to aerosol.

(3) Deposition is a mix of local and distant sources. Deposition collected passively on a surface or actively in a plant normally accumulates for months to years before it is sampled. Both dry and wet components of this long-term deposition are the sum of multiple events, each of which represents a different mix of local and distant sources. Ideally, only sources within the first 200-500 km should be used to generate signatures, but this is not possible for deposition in the way it is for aerosol, where we can exclude samples with distant influences.

(4) Wet deposition is skewed to distant sources. The wet component of deposition is more weighted toward distant sources than aerosol is. This effect has been known for years but never widely publicized. We recently encountered it in our study of rain in Narragansett, where elemental proportions in rain and aerosol differ by factors of 1.3-1.8. Narragansett may be an extreme case, however, for elemental proportions in the Northeast differ from those of the neighboring Midwest by factors of up to nearly 200, which is much larger than in most other cases we have dealt with.

(5) Differential leaching from accumulating deposition. Because deposition on a surface accumulates for months to years before being sampled, it is washed by many rains. As a result, the proportions of elements having different solubilities may be altered.

Is there any hope for using deposition as a surrogate for aerosol? The answer depends on the magnitudes of the perturbing effects listed above. Although definitive information is not yet available, preliminary data from our studies in Narragansett can be combined with the scanty literature to give a cautiously optimistic picture. The next paragraphs show that proportions of fine-particle elements in deposition at Narragansett are generally within a factor of two of proportions in Narragansett aerosol, and within a factor of four of regional signature nearest Narragansett. (By contrast, elemental proportions

13

in the first region west of Narragansett, the Lower Midwest, differ by factors of as much as 170 from Narragansett's local signature.) The paragraphs below also show that in the best experiment to date, fine-elemental proportions in lichens and ambient aerosol differed by factors of only 3.4 or less (even though this experiment was not optimized). Thus, it seems justified to investigate both wet deposition and biodeposition further as potential surrogates for aerosol.

Table 2 presents the summary of our elemental data for Narragansett on which the above conclusions are based. The upper portion of the table lists the signatures of the Lower Midwest (LMW) and the Central East Coast (CEC) as elemental ratios to Se, and corresponding values of these same elemental ratios in average Narragansett aerosol (summer 1982 and winter 1982-83, as reported in Science by Rahn and Lowenthal, 1985) and average wet deposition at Narragansett (1985-86, as generated under our DOE Grant). The lower portion of the table expresses these same data as ratios of the ratios to CEC. It should first be noted how much the local signature CEC and the upwind signature LMW differ - by factors of 3-170. By contrast, average Narragansett aerosol, which is a mixture of local and distant contributions, differs much less from CEC - by factors of only 0.6-1.9, i.e., by a factor of two at most. And lastly, average wet deposition at Narragansett - which we have found to be skewed toward distant sources relative to aerosol - differs from the local signature CEC by factors of 0.9-3.5, or by a factor of four at most. Not shown here but easily derived is that wet deposition at Narragansett differs from local aerosol by factors of two or less. Thus, elemental proportions in deposition at Narragansett agree within a factor of two with proportions in aerosol, and within a factor of four with the local signature.

What then about biodeposition? How closely does deposition measured in plants resemble the local aerosol or the local signature? We have surveyed the literature and find no clear picture emerging. On closer inspection, however, we have decided that the picture is rosier than often thought, and that there is reason to believe that certain plants can monitor elements in deposition nearly as reliably as we can in wet deposition.

The literature contains several scattered reports by various groups on trace elements in mosses, lichens, bark, leaves, etc. Most do not offer corresponding analysis of the parent aerosol. In one case, however, we were able to compare mosses from Norway, as analyzed by Eiliv Steinnes of the Norwegian Institute for Atomic Energy, with our earlier data on aerosol from northern Norway. The results were too scattered to be useful, probably because the mosses were sampled in different years and at different places than the aerosol was.

Recently, though, a set of data was published which is much more encouraging. Olmez et al. (1985) measured elemental concentrations in lichens near the Dickerson coal-fired power plant in Maryland. They tried to interpret the data in terms of size-segregated aerosol from the general region, and came up with a confusing result. We have re-interpreted their data by using only total aerosol from nearby NBS (Kowalczyk et al., 1982) for comparison, and got a more-sensible result. Figure 2 shows this comparison, as a scatter diagram of

14

Table 2. Elemental ratios in signatures, aerosol,
and wet deposition at Narragnsett, RI

	Lower Midwest signature (LMW)	Central East Coast signature (CEC)	Avg. aerosol summer 1982, winter 1982-83	Avg. wet dep. 1985-86
As/Se	0.23	0.74	0.63	0.84
Sb/Se	0.148	1.14	0.77	0.45
Noncr.V/Se	0.160	27	14.2	7.8
Zn/Se	5.3	29	20.5	-
In/Se(x10³)	1.0	4.6	7.1	-
Noncr.Mn/Se	1.10	3.7	2.7	-

	CEC/LMW	CEC/Narr. aer.	CEC/Narr. dep.
As/Se	3.2	1.17	0.88
Sb/Se	7.7	1.48	2.5
Noncr.V/Se	169	1.90	3.5
Zn/Se	5.5	1.41	-
In/Se	4.6	0.65	-
Noncr.Mn/Se	3.4	1.37	-
	3-170	0.6-1.9	0.9-3.5

15
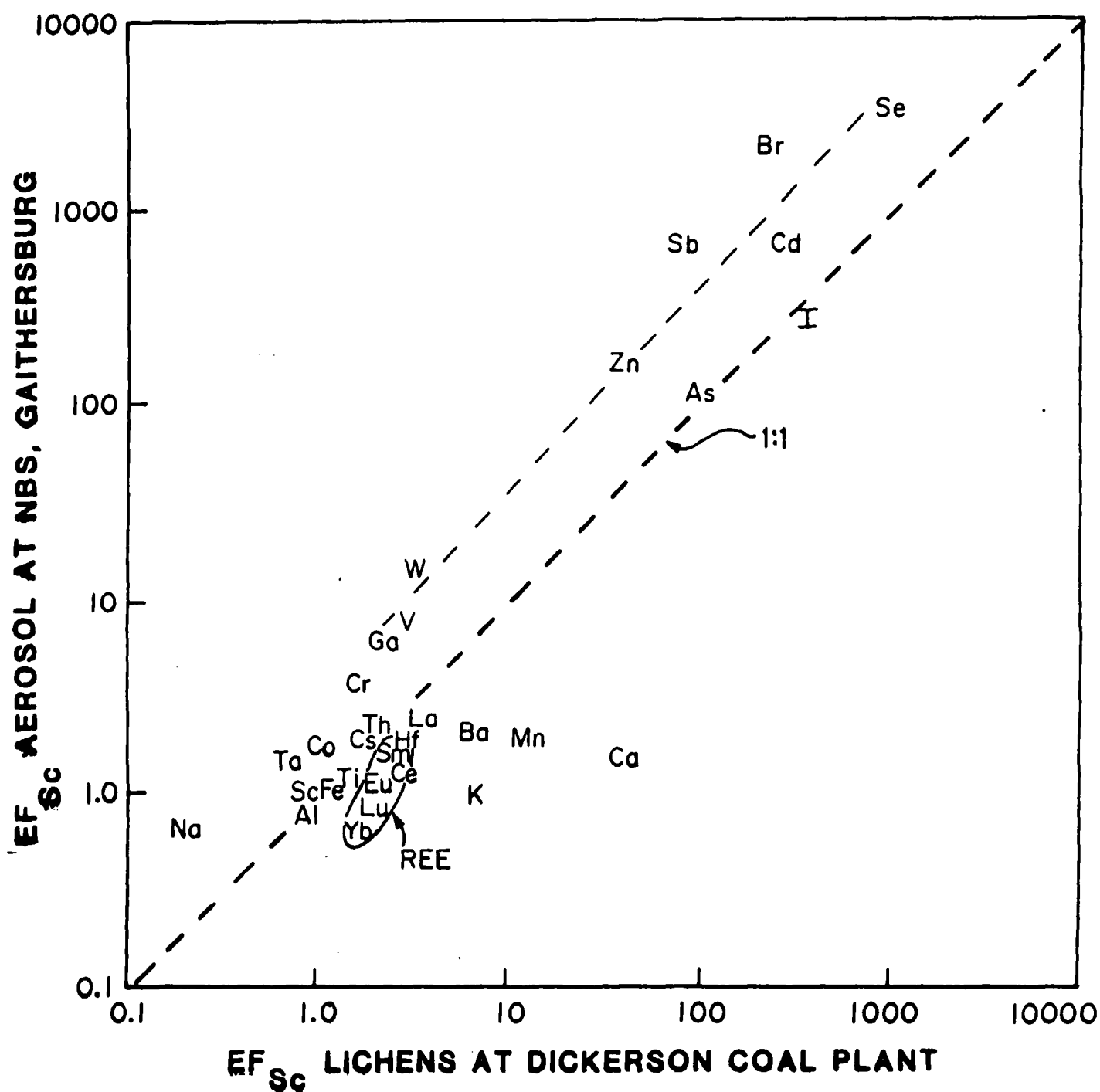
Figure 2. Scatter diagram of crustal enrichment factors of trace elements in aerosol and lichens in southern Maryland. Note similar proportions of most pollution elements (upper line) in both media.

aerosol-crust enrichment factors of elements in lichens near Dickerson vs. enrichment factors in aerosol near NBS. The form of the plot is clear: lithophilic elements such as Al, Sc, Fe, and the rare earths are not enriched in either medium, a few essential elements such as Ca, K, and Mn are an order-of-magnitude more enriched in lichens than in aerosol, and a large number of pollution-derived elements such as Ga, Cr, V, W, Zn, As, Sb, Cd, and Se are depleted several-fold in lichens relative to aerosol. This last feature appears on the plot as a 45° line displaced upward from the 1:1 line by about a factor of four.

Thus, the nonessential elements form two distinct groups, the crustal ones which are in the same proportions in aerosol and lichens and the pollution-derived ones which are depleted in lichens by a factor of four. Within the pollution-derived elements, however, the proportions are similar between aerosol and lichens. Therein hangs the key to the potential of lichens as bioindicators, for our tracer system is really only concerned with the fine-particle, pollution-derived elements. How they are fractionated as a class relative to the crustal elements does not matter as long as they are not fractionated within themselves.

To evaluate the degree of fractionation within the tracer elements more quantitatively, we have constructed Table 3, which shows X/Se ratios in the NBS aerosol and the lichens near the Dickerson coal plant. The last column gives the ratio of the X/Se ratios in the two media, and shows that elemental proportions differed by factors of 1.16-3.4, i.e. by less than a factor of four. The significance of this result is that the elemental relation between lichens and aerosol in Maryland, better than a factor of four, is only marginally worse than the relation between wet deposition and aerosol at Narragansett, better than a factor of two. In fact, the true relation between aerosol and lichens in Maryland may be better than shown in Table 3, for the data are not optimal, because aerosol was only sampled for eight weeks, and that was during a period of unusual dryness and high pollution. The definitive experiment linking aerosol and lichens, wet deposition and lichens, or all three has never been done, and might give significantly better results than any of the partial data to date.

We are in a position to conduct the complete experiment. We have abundant elemental data on aerosol and wet deposition at Narragansett, and the area is rural enough that mosses and lichens can be found in abundance. We know the literature and have considerable experience with fractionation of elements between media. Most importantly, we are highly motivated, for we stand to benefit greatly from any alternative way to generate regional signatures. As described in the Proposal section of this report, we believe that we can learn a lot about biodeposition with a relatively small effort during the next three years.

We have already looked into biodeposition a bit, beginning with pine needles, which had been suggested to us by NOAA as retaining radioactivity unusually efficiently. We found them to be unsatisfactory for trace elements: needles from Narragansett showed no enrichment of trace elements due to the atmosphere. In the course of things we will investigate grass clippings, bark,

Table 3. Elemental ratios in aerosol and lichens in Maryland

	Aerosol near NBS, August-Sept. 1976[1]	Lichens near Dickerson power plant, spring 1978[2]	Lichens/aer. or aer./lichens
As/Se	1.07	3.6	3.4
Sb/Se	0.79	0.32	2.5
V/Se	6.5	7.7	1.18
Zn/Se	67	58	1.16
Mn/Se	10.7	220	21

[1] Kowalczyk et al. (1982)
[2] Olmez et al. (1985)

18

and the bases of needles, but are not optimistic about detecting many tracer elements over the plants' background.

We have also begun to look into swipe samples of deposition from windows and other surfaces in urban areas (grime), which seems to be much more promising than pine needles. Swipe samples have long been used for measuring radioactivity, but we are not aware that they have been used for trace elements. Swipes have at least three potential limitations: (1) the need to take samples from urban areas where the deposition is heavy but possibly not regionally representative, (2) the amount of "processing" of deposited aerosol before we sample it, during which time soluble material may be leached out, and (3) high variability of swipes from different surfaces. On the other hand, windows and surfaces have the advantage of integrating deposition over days to weeks; one deposition sample is thus equivalent to several aerosol samples.

Our first experience with swipes was generally optimistic. Blank 47-mm filters of Whatman No. 41 cellulose, the same material that we use for sampling aerosol, were rubbed on the outside surface of a window in midtown Manhattan, approximately 10 stories above street level, in early spring 1986. After correcting for the material in the filter itself, the masses of the elements on the two filters were found to be in very similar proportions. Table 4 shows this for 20 elements: while the masses were about 30% greater on swipe 2, ratios of the elements to Se averaged only 6% greater on that swipe. Thus, replicate samples from a given window can agree quite satisfactorily. As this was only a preliminary test, we do not yet know how similar the material on different windows is.

But do these swipe samples compare reasonably to aerosol in Manhattan? They do, and that is encouraging, considering the preliminary nature of this experiment. Table 5 compares the X/Se ratios of one of the swipe samples to X/Se ratios for New York City aerosol of winter 1977-78, also sampled in midtown Manhattan and at roughly the 14th floor. The proportions of As, Sb, noncrustal V, and possibly also In were within a factor of 2-3 in swipe and aerosol; Se was depleted in the swipe by factors of 2-4 relative to these elements; and Zn and noncrustal Mn were enriched in the swipe by factors of 5-7 compared to the other elements. Considering that processed deposition from a single window was compared to suspended particles from an entire winter nine years earlier, the results are similar enough that we will continue to examine the swipe method.

The next experiments with swipes will center around the degree of reproducibility from surface to surface, whether the results of repeated sampling converge on signatures determined from aerosol, and whether swipes outside large metropolitan areas can be used. Swipe samples will be taken in New York City and Narragansett.

11. Tracer system extended to precipitation (under DOE grant)

For the last 18 months, we have been laying the groundwork for extending our tracer system to precipitation under a grant from DOE. To do this, we had to develop a method for sampling precipitation and analyzing it routinely for more

19

Table 4. Comparison of elemental masses in two swipe samples from an exterior window in midtown Manhattan

Element	Mass, ng		X/Se		$(X/Se)_2/(X/Se)_1$
	Swipe 1	Swipe 2	Swipe 1	Swipe 2	
Sc	30±2	42±3	0.88	1.02	1.16
Cr	1730±100	1840±110	51	45	0.88
Fe	157,000±9000	230,000±20,000	4620	5610	1.21
Co	270±20	260±20	7.9	6.3	0.80
Ni	2000±400	2900±400	59	71	1.20
Zn	27,000±2000	24,000±2000	790	590	0.75
As	97±6	140±8	2.9	3.4	1.17
Se	34±5	41±5	1.00	1.00	-
Mo	94±16	139±17	2.8	3.4	1.21
Ag	56±8	38±8	1.65	0.92	0.56
Sn	2200±100	2400±200	65	59	0.91
Sb	108±6	177±11	3.2	4.3	1.34
Cs	9.6±2.2	12.0±2.1	0.28	0.29	1.04
La	162±10	260±20	4.8	6.3	1.31
Ce	280±20	420±20	8.2	10.2	1.24
Sm	31±2	44±3	0.91	1.07	1.18
Eu	6.4±0.4	5.4±0.5	0.19	0.13	0.68
Yb	5.7±0.9	8.0±0.9	0.17	0.20	1.18
Au	11.9±0.7	16.9±1.0	0.35	0.41	1.17
Th	28±2	36±2	0.82	0.88	1.07
					1.06±0.23

Table 5. X/Se ratios in deposition (swipe) and aerosol of midtown Manhattan

	Single swipe, spring 1986	25 semi-weekly aerosol samples, winter 1977-1978	Swipe/aerosol
As/Se	2.9	0.84	3.5
Sb/Se	3.2	1.65	1.9
Noncr.V/Se	34	16.4	2.1
Zn/Se	790	57	14
Noncr.Mn/Se	53	5.1	10.4
In/Se	<0.015	0.011	<1.4

elements, at greater sensitivity, and with smaller losses than had been done before. Then we had to determine whether any of the tracer elements were fractionated between aerosol and precipitation, so that signatures for aerosol could be adjusted before they were applied to precipitation.

In spring 1986, the system finally came together and is now workable. We collect 500-700 ml of precipitation directly in clean plastic bags, then get rid of the water by freezing and freeze-drying. We then analyze the bags plus residue by neutron activation in a fashion very similar to that for aerosol. By collecting this much sample -- several times more than is common in precipitation studies -- we get as much mass as with aerosol, and thereby assure that our analysis will be nearly as good. (In practice, we can determine 20-30 elements in precipitation, as opposed to 30-40 in aerosol.) By never removing the sample from the bag, we guarantee that no material is lost by handling. Literature studies of freeze-drying show that this step loses less than 10% of all our tracer elements; we are now checking this independently. Based on more than one years of samples, we can now state that at least in Narragansett, Rhode Island, the four tracer elements As, Se, Sb, and V appear to be unfractionated by cloud-physics processes as they are incorporated from aerosol into precipitation. This means that they can be used directly to trace the origins of precipitation, without correcting aerosol signatures. (The other three tracer elements are much less useful for precipitation. Indium is rarely detected in rain and snow at Narragansett, because the enrichment of coarse-particle elements such as Na and Cl masks it. Noncrustal Mn is also masked in precipitation, presumably by the enrichment of crustal Mn. Zn has been behaving erratically enough in precipitation -- for reasons unknown -- that we do not trust our data.

The regional apportionments of precipitation at Narragansett make good sense environmentally. They indicate that precipitation derives its contaminants from systematically more-distant sources than surface aerosol does. In practice, that means that acid rain at Narragansett comes more from the Midwest than aerosol does. In Narragansett aerosol, for example, 50% of the sulfate comes from the Midwest and 50% from the Northeast. But in Narragansett precipitation, roughly 75% of the sulfate comes from the Midwest, and only 25% from the Northeast. Vertical stratification of the atmosphere seems to be causing this shift in sources, with precipitation responding to more-distant sources because it is formed aloft where air masses have not recently contacted the ground. To the best of our knowledge, this is the first time that anyone has been able to express this vertical stratification quantitatively. Everyone suspected that it took place, but no one could say how large the effect might be.

We expect that these results will eventually have legislative significance, for a control strategy where distant sources contribute only 50% of the sulfate and acidity may be quite different from one where distant sources contribute 75%.

Our precipitation work is now being recognized by other agencies. DOE, whose funding was set to lapse this fall, is about to give us a small supplement which should allow us to take on a new graduate student, our first in the area of precipitation. The Hudson River Foundation has recently funded Dr. Roy

22

Heaton for a year's work near West Point. EPA has just funded us for a two-year continuation of the DOE work.

The significance to ONR of this precipitation study is that we appear to be able to handle precipitation as clean as expected for Arctic glaciers without extreme difficulties. According to our most recent estimates, we should be able to successfully measure 14-20 elements in pre-industrial ice from Greenland (which is probably considerably cleaner than the ice core from Nordauslandet that we will be analyzing during the next three years): Na, Al, Cl, Ca, Sc, Ti, V, Mn, Fe, As, Se, Br, Sb, and I seem definite and Mg, Co, Cu, Zn, Ba, and La are potential. It is gratifying that the "definite" elements include comparable numbers of representatives from the three major classes of sources: the crust (Al, Sc, Ti, Fe), the sea (Na, Cl, Ca, Br, I), and pollution (V, Mn, As, Se, and Sb). Note that the pollution group includes five of our seven tracer elements. So we are cautiously optimistic, and will be transferring the first samples of the Nordauslandet core from Grenoble to Rhode Island later this year. Roy Heaton, our DOE investigator, will help us with the first ice analyses.

NEW REGIONAL SIGNATURES OF IMPORTANCE TO THE ARCTIC

12. Central USSR

Much of the time, Arctic aerosol is different from that found in North America, Western Europe, Eastern Europe, and China. During the past three years, we have compiled considerable chemical and meteorological evidence that its source is the Central Soviet Union, roughly the southern Urals and vicinity. The ferrous, nonferrous, and oil imprints on the aerosol match known processes in this area, air-mass trajectories point directly there as well, and even data generated within the Soviet Union from a background site in northern Kazakhstan fit key aspects of our profiles from the Arctic.

Based on these facts, we have used selected samples from the Alaskan Arctic, the Norwegian Arctic, and aircraft flights near the Taymyr Peninsula to generate a provisional elemental signature of the Central USSR. It and the justification for it were published by Lowenthal and Rahn (1985) in the special Arctic issue of Atmospheric Environment, a copy of which is included in the Appendix.

Unfortunately, this important signature had to be determined entirely outside the USSR, for the Soviet Union has been unwilling to cooperate with us on understanding the sources of Arctic haze better. We are not completely comfortable with indirect signatures like this, even though previous experience suggests that if determined carefully, they can be more reliable than one might think. We are therefore continuing to try to begin a cooperative study with the USSR on their territory, as described in Section 29 below. We are also trying to confirm this signature at other sampling sites such as Okushiri Island (Section 30).

13. Western USSR

The above-mentioned signature of the Central Soviet Union showed us that the Soviet Union was a major source of Arctic aerosol. Once we realized this, it became important to delimit the geography of this signature as much as possible, i.e., to see whether other parts of the Soviet Union had the same or different signatures.

The one thing we were prepared to do immediately was to examine the Western Soviet Union, by means of filters taken earlier for us at Ähtäri, in southern Finland. Several times per year, air masses move into this area from the Western Soviet Union, in pathways which pick up minimal interferences from Finland itself. During 1982, the Finnish Meteorological Institute had taken one year of daily filter samples for us. To derive a signature of the Western Soviet Union, we examined meteorological maps for this period and chose two periods of sustained flow from the east and southeast, and analyzed the corresponding samples. Results from the two periods agreed closely. Table 6 shows the resulting WUSSR signature, along with six others which we have used in the Arctic. This table is taken from an article soon to appear in the proceedings of the International Symposium on Arctic Atmospheric Pollution, held in Cambridge England, 2-5 September 1985 (Rahn and Lowenthal, 1986).

The WUSSR signature differs considerably from the CUSSR signature, and is not collinear with it in practical applications. In the Cambridge article, we used WUSSR with considerable success to understand transport of aerosol to the Norwegian Arctic during AGASP I. Aerosol from the Western Soviet Union is not so evident at Barrow, Alaska, however.

Incidentally, the flow which brings WUSSR to Ähtäri is very similar to that which brought the first pulse of radioactivity from Chernobyl to Scandinavia.

14. Northeastern China

China is also a potentially large source of Arctic haze. To learn about the composition of Chinese aerosol, we have been involved in a cooperative program with Chinese scientists since 1983, partially sponsored by ONR. In September 1983, K. Rahn visited China for three weeks with a People-to-People delegation on air pollution. While in Beijing, he made contact with Mr. Zhao Dianwu of the Institute of Environmental Chemistry, who ultimately supplied us with a small suite of samples from the Beijing-Tianjin area. We analyzed them for trace elements, constructed a preliminary signature from the most appropriate ones, and presented it for the first time at the Cambridge meeting. This signature, called CHINA, is also given in Table 6. The Chinese signature differs from WUSSR and CUSSR, and has led us to tentatively conclude that China is probably not an important source of Arctic haze (the same as we had concluded earlier from meteorology alone).

Our cooperation with Mr. Zhao continues, and is described in more detail below.

24

Table 6. Current regional elemental signatures for use in the Arctic
(after Table 1 of Rahn and Lowenthal, 1986)

	CEC(N=12)	MW(N=7)	UKS(N=11)	EUR(N=5)
As	0.74+0.34	2.6+0.4	1.74+0.48	3.7+0.6
Sb	1.00+0.30	1.00+0.30	1.00+0.29	1.00+0.36
Se	1.03+0.45	4.4+0.9	1.16+0.34	2.2+1.0
Noncr. V	26+10	1.54+0.17	6.7+2.0	11.2+5.0
Zn	28+11	46+4	44+11	106+44
Noncr. Mn	3.4+1.2	11.8+1.7	7.8+2.2	5.4+2.8
In(x10^3)	4.0+2.9	7.9+0.4	14.9+8.5	-

	WUSSR(N=14)	CUSSR(N=5)	CHINA(N=5)
As	3.0+0.7	10.0+0.6	2.9+1.1
Sb	1.0+0.3	1.00+0.28	1.0+0.3
Se	0.86+0.19	1.03+0.48	1.92+1.13
Noncr. V	24+13	6.5+2.0	0.48+0.09
Zn	50+25	45+16	77+29
Noncr. Mn	10.5+4.9	4.4+1.3	16.6+9.2
In(x10^3)	9.6+4.7	-	27+14

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CEC   = Central East Coast
MW    = Midwest
UKS   = United Kingdom (from Sweden)
EUR   = Europe
WUSSR = Western Soviet Union
CUSSR = Central Soviet Union
CHINA = Northeastern China
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25

APPLICATIONS OF THE TRACER SYSTEM

15. Sources of Arctic haze during a typical winter quantified

A suite of 100 daily samples from winter 1979-80 at Barrow, Alaska was completely analyzed for trace elements, then apportioned into contributions from various regional sources with the seven-element tracer system. This was the first systematic application of this system to the Arctic. (Recall that the original impetus for developing the tracer system was to understand sources and transport of Arctic haze.)

After considerable effort, it became clear that the USSR (as represented by the CUSSR signature) was contributing about 70% of the mass of the tracer elements and about 40-50% of the sulfate. Europe contributed most of the rest; North America seemed to be an unimportant source whose contribution was lost in the noise of Eurasian influences: North American sources were consistently apportioned only a few percent of the mass of the tracer elements.

The results for sulfate were less straightforward, however. On the first pass, a full 36% of the sulfate at Barrow was assigned to North American sources. We did not believe this result, because we had never seen a case where sources of sulfate differed so dramatically from sources of tracer elements, nor could we think of a reason why they should, especially when aerosol from all sources were highly aged. We therefore removed North American sources from the apportionment of sulfate, and got comparable contributions from Europe and the Soviet Union.

(This problem with collinearity illustrates that our work with the tracer system is not yet done. We have done many exciting things with seven elements, both in the Arctic and in eastern North America. But we have now reached the point where seven elements are no longer adequate - more must be added in order to reach the level of discrimination we need. The improved tracer system will be of value both for Arctic purposes and in general, for it is not yet known how many additional regional sources will be resolved by the additional elements we propose - noble metals and several from atomic absorption. See Sections 8 and 9 above for a fuller discussion of additional tracer elements.)

The results for Barrow are given in a paper by Lowenthal and Rahn in the special Arctic issue of _Atmospheric Environment_, December 1985. They form the first objective evidence that Eurasian sources dominate Arctic haze, and confirm our earlier ideas based on more indirect and subjective evidence (Rahn, 1981, "Relative importances of North America and Eurasia as sources of Arctic aerosol").

Because the new WUSSR signature, generated after Lowenthal and Rahn (1985) was submitted, appeared so promising, we reapportioned the 100 Barrow samples of winter 1979-80 using it, CUSSR, and EUR. A summary of the results was given in the Cambridge article of Rahn and Lowenthal (1986), and is given here as Table 7. In general, the contributions of CUSSR remained similar to those of

26

Table 7. Average regional apportionments of elements in the
Barrow aerosol of winter 1979-80, three sources
(after Table 3 of Rahn and Lowenthal, 1986)

| | Apportionment, pct. of mean pred. | | | Mean pred. | Mean obs. | Mean |
	EUR	WUSSR	CUSSR	ng m^{-3}	ng m^{-3}	obs./pred.
As	4.6±1.1	2.8±0.6	93±2	0.86±0.02	0.85	0.95±0.15
Sb	10.8±2.7	8.2±1.9	81±4	0.099±0.005	0.123	1.37±0.64
Se	21±5	6.2±1.4	73±5	0.113±0.009	0.102	1.17±0.96
Noncr.V	14.3±3.6	23±6	62±3	0.83±0.06	0.54	0.65±0.17
Zn	22±5	7.8±1.8	71±4	5.2±0.4	4.8	0.87±0.19
Noncr.Mn	11.6±3.0	17.2±4.1	71±4	0.49±0.03	0.70	1.69±2.12
Nonmar.SO$_4$	27±4	16.0±2.3	57±2	1330±60	1180	1.11±0.78

27

Lowenthal and Rahn (1985) or increased slightly. WUSSR, however, was given roughly one-half the previous European and North American apportionments. As a result, the total contributions from the Soviet Union rose to 79-96%. With this combination of signatures, sulfate behaved similarly to the other constituents (i.e., 84% from the Soviet Union). Thus, the new WUSSR signature indicated that during winter 1979-80, the Soviet Union seemed to be responsible for 80-95% of the mass of pollution elements in the Barrow aerosol.

This result is extremely important environmentally and politically. During the next three years of this ONR Contract, we will try to verify it in as many ways as possible, for we are aware of its volatile implications. Our various approaches will include:

- See how additional elements affect the regional apportionments.
- Analyze and apportion other winters at Barrow.
- Examine the stability of our apportionments by mathematical simulations.

16. Direct anthropogenic effect on pulses of CO_2 in Alaska found by means of tracer system

It is now generally accepted that atmospheric CO_2 has been increasing anthropogenically since the Industrial Revolution, and is now 20-25% more concentrated than in pre-Industrial times. In spite of this, direct evidence on anthropogenic contributions fo CO_2 are very few in number, largely because CO_2 has been studied primarily in remote areas where natural variations easily mask the anthropogenic signal. The problem of differentiating between anthropogenic and natural CO_2 is not unlike that of differentiating between regional contributions to sulfate, for both CO_2 and sulfate from different sources look identical, and when either is studied alone, the different contributions cannot be unraveled easily.

For some years, we have known that regular pulses of CO_2 appear at Barrow, Alaska several times each winter. They are up to 3 ppm above the winter background of 340 ppm, and last 1-5 days (Peterson et al., 1982; Halter and Harris, 1983). Our work under this Arctic Haze Contract has shown that pollution aerosol at Barrow, in addition to having a high winter background, also arrives in distinct pulses reminiscent of those for CO_2.

Could the two sets of pulses be related, or even simultaneous, i.e., different expressions of a common underlying transport of polluted air masses? We addressed this in cooperation with Brad Halter and Joyce Harris of the NOAA Geophysical Monitoring for Climatic Change Program in Boulder, Colorado, the office which operates the baseline observatory in Barrow from which we have obtained so many aerosol samples during the last decade. By using their data for CO_2 and ours for elements in aerosol during winter 1979-80 at Barrow (the same samples apportioned regionally by Lowenthal and Rahn, 1985), we were able to find that many of the pulses of CO_2 were indeed correlated with pulses of pollution aerosol. To the best of our knowledge, this was the first demonstration of a direct anthropogenic effect on CO_2 of remote regions, and represents a major success for elemental tracers. Our findings appeared in an article by

B.C. Halter, J.M. Harris, and K.A. Rahn in the December 1985 Arctic issue of _Atmospheric Environment_ entitled "A study of winter variability in carbon dioxide and Arctic haze aerosols at Barrow, Alaska" (Halter et al., 1985).

The major conclusions cited there are worth reproducing here, because they are quite wide-ranging and exemplify the broad application that elemental tracers will find in the future:

"The following conclusions may be drawn concerning the winter of 1979-1980 at Barrow:
1. Pollution sources in the western half of Eurasia made the most important contributions to periods of elevated CO_2 concentration.
2. Transport of the greatest amounts of pollution CO_2 to Barrow was by air streams coming across the Arctic Basin from Europe or western U.S.S.R. in 10 days or less.
3. Arctic regional background CO_2 concentrations had a pollution component.
4. Three air pollution situations influenced CO_2 concentration:
   (a) Direct transport of pollution CO_2 from western Eurasia;
   (b) polluted Arctic background;
   (c) dilution of polluted Arctic background by intrusion of Pacific air aloft.
Recognition of the three associated ranges in CO_2 concentration may prove useful in selecting data from the Barrow record for use in studies of CO_2 trends in the Arctic."

17. Sources of Arctic aerosol during AGASP I quantified

After we had shown that our elemental signatures resolved sources of Barrow aerosol during winter 1979-80, we applied them to sources of aerosol during AGASP I of March-April 1983. Because samples from the aircraft itself were shorter and flow rates were considerably smaller than we had expected, they proved extremely difficult to analyze, and have given mixed results. Samples from the ground proved much more tractable, however.

We received two sets of ground-based filters during AGASP I, from Barrow, Alaska and Ny-Ålesund, Spitsbergen. Those from Barrow were daily; those from Ny-Ålesund were taken in weekly sequences of 2,2,3 days. NOAA/GMCC provided the filters from Barrow, Dr. B. Ottar of the Norwegian Institute for Air Research provided filters from Ny-Ålesund. We analyzed all samples for sulfate and trace elements, and reported the results at the International Symposium on Arctic Atmospheric Pollution in Cambridge, England, 2-5 September 1985 (Rahn and Lowenthal, 1986). We also reported the new WUSSR and CHINA signatures there, as noted in earlier sections of this report.

By chance, a major pollution episode occurred during March 1983, and was captured by AGASP I on both sides of the Arctic. This episode formed a major part of AGASP I, and provided a fine example of how the Arctic is ideally suited for chemistry and meteorology to work together to explain events which might otherwise be intractable. The episode was observed during the second week of March at the surface in Ny-Ålesund, Spitsbergen and a few days later aloft and at the surface in Barrow, Alaska.

29

We analyzed 13 samples from Ny-Ålesund covering 4 March-1 April 1983, and 22 samples from Barrow covering 2-27 March 1983. Each set was apportioned into contributions from EUR, WUSSR, and CUSSR. At Ny-Ålesund, the episode came strongly from the central Soviet Union and lasted from 7-14 March. European aerosol was practically absent, but aerosol from the western Soviet Union rose quickly to a gentle maximum and declined steadily thereafter. Meteorological maps showed that the big pulse of aerosol from the central Soviet Union was clearly linked with a classical "return-flow" pathway; the early pulse from the western Soviet Union was caused by the leading edge of the low moving rapidly toward the Urals and temporarily propelling air from the western Soviet Union first north, then west. Aerosol from Europe moved eastward and southeastward, however. The smaller episode of 21-28 March began with a pulse from the central Soviet Union, followed by a larger pulse from the western Soviet Union, then concluded with another pulse from the central Soviet Union. The origin of all these pulses could be seen clearly in the meteorological maps for the period.

At Barrow, the big episode was seen 12-19 March 1983. This episode had two clearly defined phases: three days strongly from the central Soviet Union followed by five days of more mixed character in which the coefficient of the central Soviet Union decreased by a factor of two while those of Europe and the western Soviet Union remained roughly constant. Our analysis of aerosol samples from the haze layers aloft near Barrow early on the 12th and 14th, taken with the AGASP aircraft, show that they were also dominated by aerosol from the central Soviet Union (their As/Sb ratios were 8-17).

The aerosol of the first phase was transported from the central Soviet Union by the same low-pressure area which affected Ny-Ålesund. Once in the Arctic, however, the two paths diverged, with the Ny-Ålesund aerosol continuing around the low but the Barrow aerosol coming under the influence of a large high-pressure area centered over the Chukchi Peninsula. During the first days of the episode, this high moved toward Barrow and cut off direct transport from the central Soviet Union, thus decreasing its coefficients. Aerosol of the second phase of the episode can therefore be viewed as residue from the big pulse mixed with smaller, more normal contributions from other sources which affect the Arctic, such as Europe and the western Soviet Union. North American and other Asian sources might also have contributed during this period; our tracer system is not yet sophisticated enough to resolve such complex mixtures as these, especially at the low concentrations seen here. On AGASP Flight 3, early in 16 March, the aerosol aloft did indeed appear to be European rather than from the central Soviet Union (As/Sb ratios of 3). The episode ended around the 20th or 21st, when the high-pressure area had advanced far enough east to cut off Barrow completely from transported aerosol.

The average elemental apportionments for the Barrow aerosol of March 1983 among the European and Soviet Union signatures are shown in Table 8. The results are quite similar to those of winter 1979-80, but with the European contribution being 10-30% greater.

AGASP I shows how we are presently fusing chemical and meteorological techniques in the Arctic to a degree seldom seen elsewhere. Patterns of interaction

30

Table 8. Average regional apportionments of elements in the
Barrow aerosol of March 1983, three sources
(after Rahn and Lowenthal, 1986)

| | Apportionment, pct. of mean pred. | | | Mean pred. | Mean obs. | Mean |
	EUR	WUSSR	CUSSR	$ng\ m^{-3}$	$ng\ m^{-3}$	obs./pred.
As	15.9+2.5	5.0+1.4	79+3	1.37+0.06	1.39	1.00+0.02
Sb	31+5	12.0+3.5	57+5	0.189+0.015	0.25	1.27+1.25
Se	50+10	7.5+2.2	43+5	0.26+0.03	0.172	0.70+0.19
Noncr.V	35+7	29+9	37+3	1.90+0.22	1.58	0.81+0.18
Zn	51+9	9.2+2.9	40+4	12.3+1.3	15.7	1.26+0.30
Noncr.Mn	31+6	23+7	46+4	1.03+0.11	1.17	1.19+0.22
Nonmar.$SO_4^=$	37+7	29+8	34+6	2200+300	2100	1.00+0.31

31

are being developed which will serve as models for the future. All this is most appropriate, for the difficulty of unravelling sources and transport of Arctic haze is so great that no single technique can realistically expect to do it all.

18. Summer haze over Alaska during July 1986

As this proposal was being finalized, we learned of an episode of haze observed over much of Alaska during July 1986, and became very curious about its origin. The first source of information was an article on the front page of the 30 July 1986 issue of the Anchorage Daily News, with a color picture of the haze seen clearly against nearby Mt. Susitna during the last week of July. The writer, John Tetpon, had contacted several scientists throughout the state, and determined that it was also seen in the Fairbanks area, and possibly at Barrow as well. Various sources suggested that it might have been industrial in origin and from Eurasia, i.e., "classical" Arctic haze, but no one could be sure. The article went on to say that if the phenomenon were indeed true Arctic haze, this would be the farthest south that it had been observed (60N).

We reacted quite differently. In light of the growing body of evidence that Arctic haze reaches central Canada regularly during winter (55N), may reach southern Washington State during winter (47N), and apparently also Okushiri Island during winter (42N), as summarized in Section 37 below, we were much less impressed by finding it in southern Alaska. Rather, the possibility of seeing Arctic haze in summer struck us as crucial, for summertime Arctic haze had not yet been documented for Alaska. We decided to look into the subject further. This investigation is now proceeding rapidly, and appears to be opening up a whole new aspect of Arctic haze. The paragraphs below summarize our initial findings.

We first called Glenn Shaw at the University of Alaska in Fairbanks and confirmed that the haze had been visible near Fairbanks during late July. In fact, he had pointed it out to a group of graduate students. We then consulted the meteorological maps, and found that during the second half of July 1986, the polar front had migrated northward to an unusual degree and allowed air to enter Alaska more rapidly and more from the west than is customary during summer. Areas ranging from Barrow to Anchorage were exposed to this flow at one time or another during the period. During summer, Barrow normally receives more-stagnant air from over the ice, and Anchorage receives air from much farther south over the Pacific. During this period, however, the air seemed to have come rather directly from northern Eurasia.

During summer, there are always forest fires in the northern continents, and we wondered whether the haze might just have been smoke. We had not seen nay report of large firest in Alaska or Siberia, however. To be sure, we contacted the National Environmental Satellite Data Information Service (NESDIS), and asked them to look over their satellite images for July. They subsequently reported to us that Siberia had only experienced scattered, minor fires during that time, without any evidence of large plumes of smoke traveling long distances. The summer had been normal or cleaner than normal. Fires could not have caused statewide haze in Alaska.

We then looked into the situation chemically. Glenn Shaw provided eight filter samples from the Fairbanks area which we analyzed. To these, we added three of our own from Barrow. The Fairbanks samples appeared not to be useful, for they were influenced too much by the city itself (they had been taken on the roof of the Geophysical Institute for Chernobyl purposes, and never intended for more stringent uses such as we tried). The Barrow samples made much more sense, however. Elemental concentrations were much lower, and more in line with those expected for summer. The concentrations and ratios of our two best tracer elements for summer, As and Sb, provided valuable clues to the nature and origin of the haze at Barrow. Concentrations were highest in the first sample, then decreased by factors of 15-30 by the third sample. Preliminary trajectories calculated by Dr. R.D. Borys suggested that the event at Barrow began only late during the first sample, roughly 18 July. We scaled the concentrations in the first (11-day) sample to what they would have been if all the As and Sb had come during those last four days, and found that they were comparable to winter-mean concentrations for Barrow. Thus, a significant pulse of industrial aerosol reached Barrow in mid-July 1986.

The As/Sb ratio is a powerful indicator of origin of pollution aerosol in the Arctic. As/Sb ratios for the three Barrow samples clearly eliminated the Central Soviet Union and the East Coast of North America as sources. Considering the general meteorology of the period, we felt that China and the American Midwest could also be eliminated. The best overall match was with As/Sb ratios of Europe and the Western USSR.

Preliminary 500-mb trajectories supported the chemical evidence that the pollution aerosol came from Europe. Dr. Borys used our German meteorological maps to calculate several trajectories by hand while he was visiting us for a week. He did them in 12-hour steps, the best that can be done by hand. In general, trajectories both to Barrow and Anchorage came from the vicinity of Europe, even though air came to Barrow most immediately from the south and to Anchorage from the north. Of course, after ten days of calculation, trajectories must be considered a guide rather than definitive. But they do agree with the chemical analysis, and seem to be a solid beginning.

Arctic haze literature contains data on mid-summer transport of aerosol to Barrow which has never been followed up properly. In 1981, John Miller of NOAA showed a peak of long-range transport to Barrow during August, apparently composed of components from both north and south. The southerly component is probably clean air from the Pacific, while the northerly component is more likely to be Eurasian and more polluted. While the magnitude of this summer transport varies from year to year, it appears to be significant on at least a five-year average. Dr. Miller presented this material at the Second Symposium on Arctic Air Chemistry in May 1980 at Narragansett. At the same symposium, Dr. Barry Bodhaine showed that Barrow has an August peak in condensation nuclei and a July-August maximum in light scattering, the latter presumably responding to a maximum in fine particles. Thus, John Miller's maximum in transport produces a real chemical effect, and is not just extra air. Light scattering at Barrow passes through a clear minimum during June, then becomes quite volatile during July and particularly August, when it oscillates between June-like and winter-

like values. It is almost as if Barrow only has a single month of truly clean
summer, after which transport begins, haltingly, to re-establish itself.

Why a maximum during July and August? It may be no coincidence that July
and August are just the times when the polar vortex is contracted to the maxi-
mum. In the continental U.S., this allows hazy, humid air from the south to
invade, bringing episodes of transported pollution in July and stagnant, local
pollution during August (associated with August's "dog days"). At Alaska's
latitudes, contracting the polar vortex brings the polar front and its asso-
ciated zone of active transport northward to the state. Much of the time, of
course, clean air is transported, but apparently, periods of transport of
dirtier air are interspersed. Thus the big oscillations reported by Bodhaine,
which are not seen any other time during the year except during November, when
flow in the midlatitudes is begining to oscillate as the winter patterns there
are becoming established.

Dr. Borys pointed out that the summer episode of 1986 was associated with a
surface high-pressure area over much of the ice pack. This would promote
transport by minimizing clouds and rain. Out of curiosity, we checked maps for
the episodes in 1978 and 1979, which were particularly strong, and found similar
meteorology. These synoptic conditions resemble those of winter, or more pro-
perly spring, to a considerable extent, and reinforce our original notion that
directed flow and minimized precipitation are the major factors responsible for
the unusually long transport of Arctic haze. Also, the spring high over the ice
cuts off flow to Barrow from the Central Soviet Union, and tends to bring more
European aerosol, just as we saw in this summer episode. Summer is not always
so different from winter.

Of course, our understanding of summer transport is still at a very early
stage. It has to be pursued both chemically and meteorologically. Chemically,
we plan to analyze more of our summer filters from Barrow, which have sat pretty
much dormant over the years. Meteorologically, we can work more with Joyce
Harris of NOAA Boulder, who will surely become very interested in this subject.

AEROSOL SAMPLING

19. Barrow, Alaska

The NOAA Geophysical Monitoring for Climatic Change Program, through its
baseline observatory in Barrow, has continued to sample aerosol for us
throughout this three-year period. Most samples have been semi-weekly, except
for special occasions when daily samples were taken. We now have nearly 10
years of samples accumulated from Barrow.

20. Iceland

The Icelandic Meteorological Office has graciously continued to take two-day
samples of aerosol for us at the power day in Irafoss east of Reykjavik.

34

21. Europe

Sampling at various sites in Western and Eastern Europe, so active during the previous three years, ceased during this three-year period. The accumulated samples, several hundred in number, continue to be a valuable resource which will be tapped steadily during the coming years. For example, we derived the signature of the Western Soviet Union in 1984 and 1985 from samples taken in Äthäri, Finland during 1982.

22. Narragansett, Rhode Island

We are continuing to take daily aerosol samples in Narragansett, as we have since 1982. These samples are used for Arctic purposes as well as for acid-rain purposes under other projects. For example, the Central East Coast signature derived from Narragansett (Rahn and Lowenthal, 1985) is used in searching for North America contributions to Arctic haze.

23. Participation in AGASP I

We participated in the NOAA/ONR Arctic Gas and Aerosol Sampling Program of spring 1983 by sampling and analyzing filters from the aircraft and the ground. In addition, K. Rahn took part in the Norwegian leg, both as consulting meteorologist and aboard the aircraft.

AGASP I was a very valuable program for us. Our major results have already been discussed in Section 17 above.

24. Participation in AGASP II

We are participating extensively in AGASP II as well:

(1) K. Rahn gave invited overview talks at the two AGASP II planning meetings of April and September 1985.
(2) K. Rahn was made Chairman of the Tracer Committee for AGASP II. In September 1985, he and R. Schnell of NOAA Boulder met with interested French scientists in Paris to discuss their participation in a possible balloon-tracer experiment during AGASP II. Ultimately, the French were unable to participate. We had also hoped that Los Alamos National Laboratory would be able to release and track their heavy-methane gaseous tracers during AGASP II as well, but they were unable to secure funding.
(3) K. Rahn was set to join the AGASP II aircraft in Thule, Greenland, but was forced to cancel when the flight schedule was revised to base it entirely in Anchorage.
(4) We have received a large set of filters from the aircraft, and are analyzing them.
(5) D. Lowenthal attended an AGASP II workshop in Toronto during October 1986, to discuss and begin to interpret the preliminary results.

THESES

25. Analysis of cascade-impactor samples from Barrow and European source regions (N.F. Lewis M.S. thesis completed)

The M.S. thesis of Noëlle F. Lewis on particle-size distributions of trace elements in Arctic aerosol, entitled "Particle-size distributions of the Arctic aerosol", was defended successfully in May 1985. This research detailed the particle-size distributions of numerous elements in Arctic haze, in its European source aerosol, and changes in these size distributions during transport from Europe to Alaska. The abstract to this thesis is included in the Appendix to this report.

Among other things, this study found that size distributions changed more during the first 1000 km of transport (from cities in central Europe to rural Sweden, for example) than during the next several thousand km to Barrow. Elemental ratios used as tracers appeared to change by 10-40% during the first 1000 km of transport, but only 0-13% after that. This implied that in our system of regional tracing, which uses elemental ratios determined regionally (after a few hundred km of transport), regional signatures should be stable to within 13% or so. Qualitatively, this result agrees with two other types of evidence we have generated: comparisons of polluted air masses before and after transport within North America in which elemental ratios change less than 25%, and comparison of elemental ratios in precipitation and parent aerosol which agree to roughly the same precision for four of six tracers. Thus, it now seems that most elemental ratios are satisfactorily stable during long-range transport.

26. Operational and statistical aspects of the tracer system (D.H. Lowenthal Ph.D. thesis completed)

The Ph.D. thesis of Douglas H. Lowenthal on operational and statistical aspects of the tracer system, entitled "Regional source apportionment and related statistical topics", was defended successfully in May 1986. It was composed of four articles which have been submitted for publication. The abstract of this thesis is included in the Appendix to this report.

Dr. Lowenthal has provided a solid mathematical and statistical basis for our regional tracer system. Without his work, the tracer system would not be operational. It is impossible to summarize Dr. Lowenthal's accomplishments in this short space. Let it be said, though, that he showed how to decide that most of our regional signatures are distinct, that tracer elements in aerosol samples can be apportioned into regional contributions with results that are stable with respect to details of calculation as well as perturbations in samples and signatures, and are environmentally meaningful.

27. K. Rahn visits PRC and begins joint program on tracers of Chinese aerosol

As noted briefly above, K. Rahn visited China in fall 1983 with a People-to-People delegation of air-pollution specialists. One of the main goals of this trip was to establish contacts with Chinese scientists and eventually get enough samples of Chinese aerosol to derive one or more regional signatures and see whether China was a source of Arctic haze. From circulation patterns in that part of the world, we thought that China probably was not a major contributor to Arctic aerosol, but we couldn't be sure.

We made contact with Mr. Zhao Dianwu of the Institute of Environmental Chemistry in Beijing, and eventually got a small series of samples from the Beijing-Tianjin area which suggested that this region was not a major source of the haze. This signature was first presented at the Cambridge Arctic Symposium of September 1985, and will appear in the Proceedings. In fall 1985, Mr. Zhao sent us an additional series of aerosol samples from three sites in southwestern China; they generally confirmed the earlier results from northeastern China.

This information on Chinese aerosol is very important in helping us answer at least three quite different questions:
- (1) whether China contributes significantly to Arctic haze,
- (2) how much China masks the CUSSR contribution at Okushiri Island (see Section 30 below for fuller discussion), and
- (3) the more general question of how similar or different pollution aerosols from various countries are.

Mr. Zhao is very keen on having this cooperation continue, for he wants to learn our elemental tracer technique and apply it to studying long-range transport in and around China. Mr. Zhao is a remarkable individual. He is the father of acid-rain studies in China, and presently serves on two national committees which oversee Chinese research in this area. Having successfully gotten this momentum going, he searched for a new field some years ago, and decided that long-range transport was the most important subject he could tackle for the rest of his career. After surveying the available techniques, he settled on ours as the most promising. This is why he is so eager to cooperate with us over the long term.

As part of our joint project, our two groups are preparing a paper on the Chinese samples we have analyzed to date. K. Rahn is also about to submit an article to Zhao to be published in the Chinese equivalent of Atmospheric Environment.

28. Chinese scientists visit our group

In November 1985, Mr. Su Weihan of the Institute of Environmental Chemistry, Beijing, visited our group for a week. After spending three months in the U.S., he is now back in China, and seems very keen on cooperating with us.

In April 1986, Mr. Zhao Dianwu, also of the Institute of Environmental Chemistry, Beijing, visited us for a week, on his way home from a UN conference on acidification of the tropical environment held in Caracas. The week was most profitable. We discussed our joint manuscript on the Chinese aerosol and how it compares with Japanese and USSR aerosols. We also discussed how to expand our cooperation, for they would like to send a researcher or a student here to learn our tracer technique. To begin, two Chinese scientists from Guizhou Province will visit here in fall 1986 or spring 1987, then K. Rahn will return the visit somewhat later.

29. K. Rahn visits USSR to plan joint program on USSR aerosol

We have been trying to get aerosol samples from the Soviet Union for several years, in order to confirm our CUSSR signature which seems to be so important to Arctic haze. The USSR's secrecy about their environment and about their Arctic has made this project very slow and frustrating. In preparation for a joint study, K. Rahn visited the USSR for two weeks during April 1984, under the auspices of Working Group VIII of the US-USSR Bilateral Agreement on Cooperation in the Field of Environmental Protection. This visit was designed to allow K. Rahn to become familiar with air-pollution laboratories in the USSR and plan a joint study of trace elements and long-range transport of US and USSR aerosols. Extensive discussions were held at Leningrad, Vilnius, and Moscow, and the study was tentatively set for late 1984 or early 1985.

Subsequently, the project was delayed unilaterally by the USSR, on the grounds that no official protocol had been signed. Attempts to work with the USSR have continued, however, because we deem the project so important. In early 1985, K. Rahn met with a Soviet delegation in Boston for this purpose, and kept the project alive even though NOAA/GMCC's attempt to involve the USSR in AGASP II was turned down flatly and abruptly. In November 1985, John Miller from NOAA Silver Spring attended a meeting in Tashkent and received informal approval for K. Rahn to visit the USSR in early 1986 to plan the experiment, which was then foreseen for summer 1986. The formal request to visit the USSR in January or February 1986 was declined by the USSR, however.

The USSR has most recently requested that our project be transferred to the recently reactivated Working Group II on Air Pollution Modeling and Monitoring, because they felt it would fit there better than under Working Group VIII, The Influence of Environmental Changes on Climate. After initially resisting this suggestion because of the additional delay it would impose, we have acquiesced, principally because we recognize the USSR's right to control the terms of any experiment on its territory. The next joint meeting of Working Group II was scheduled for 29 September 1986 in Washington; K. Rahn was invited to attend and was given 90 minutes to discuss the project. At the last minute, the USSR side postponed the meeting until March-April 1987, however.

30. Okushiri Island off Hokkaido - joint Japanese-American study of Asian pollution aerosol

Because our Central Soviet Union signature is so important, it and its origins should be verified in any way possible. Nearly two years ago, we were given information which indicated that the best place outside the Soviet Union other than the Soviet Arctic to look for this signature might be Hokkaido (northern Japan) during winter. We contacted Prof. S. Tsunogai from Hokkaido University, who agreed to arrange for six months of daily aerosol samples to be taken on Okushiri Island, just west of Hokkaido, for $1000 plus one-half of each filter (which a Master's student there would use for a thesis). The project went off without a hitch: we got 186 daily samples in a totally unbroken series between late November 1984 and the end of May 1985, the only deviation being a major snowstorm which caused one sample to run for two days. We analyzed all the filters as soon as possible after we received them.

The experiment worked very well. A great deal of pollution aerosol was found throughout the period, although the latter half of the samples were somewhat cleaner than the earlier half. The major results can be summarized as follows:

(1) Strong evidence for the signature of the Central Soviet Union, CUSSR, was indeed found. CUSSR was needed to explain both the chemical composition of individual samples with trajectories from the Central Soviet Union and the average Okushiri Island aerosol as well.

(2) A new signature, apparently from the highly industrialized Anshan-Shenyang area of northeastern China (Manchuria) was found. Like CUSSR, it was needed to explain the composition both of individual samples from Manchuria and the average aerosol.

(3) A component of aerosol with signature like those of Japan and/or China was needed to explain many aerosol samples from those directions, particularly in summer.

(4) Japanese signatures based on the two cities nearest Okushiri Island or on 16 cities over all Japan worked equally well for Okushiri aerosol.

(5) Chinese signatures based on the Beijing-Tianjin area or Beijing-Tianjin plus three cities in southwestern China worked equally well for Okushiri aerosol.

(6) Arctic aerosol appeared at Okushiri Island for a few days in mid-winter, during a single period when air came strongly and persistently from the north. The composition of this aerosol was not explained by China, Japan, or the Central Soviet Union, but rather required a European-like source. This topic is discussed more in Section 37 below.

We will begin preparing this material for publication shortly. The paragraphs below illustrate a few of the figures and tables we are assembling.

Figure 3 shows the location of Okushiri Island (at the confluence of the sectors) as well as the five sectors we selected to represent potential source areas. Sector 1 represents Japan, Sector 2 represents Korea and China, Sector 3 represents the Central Soviet Union, Sector 4 represents the extreme eastern Soviet Union and the Arctic, and Sector 5 represents Pacific sources.

39
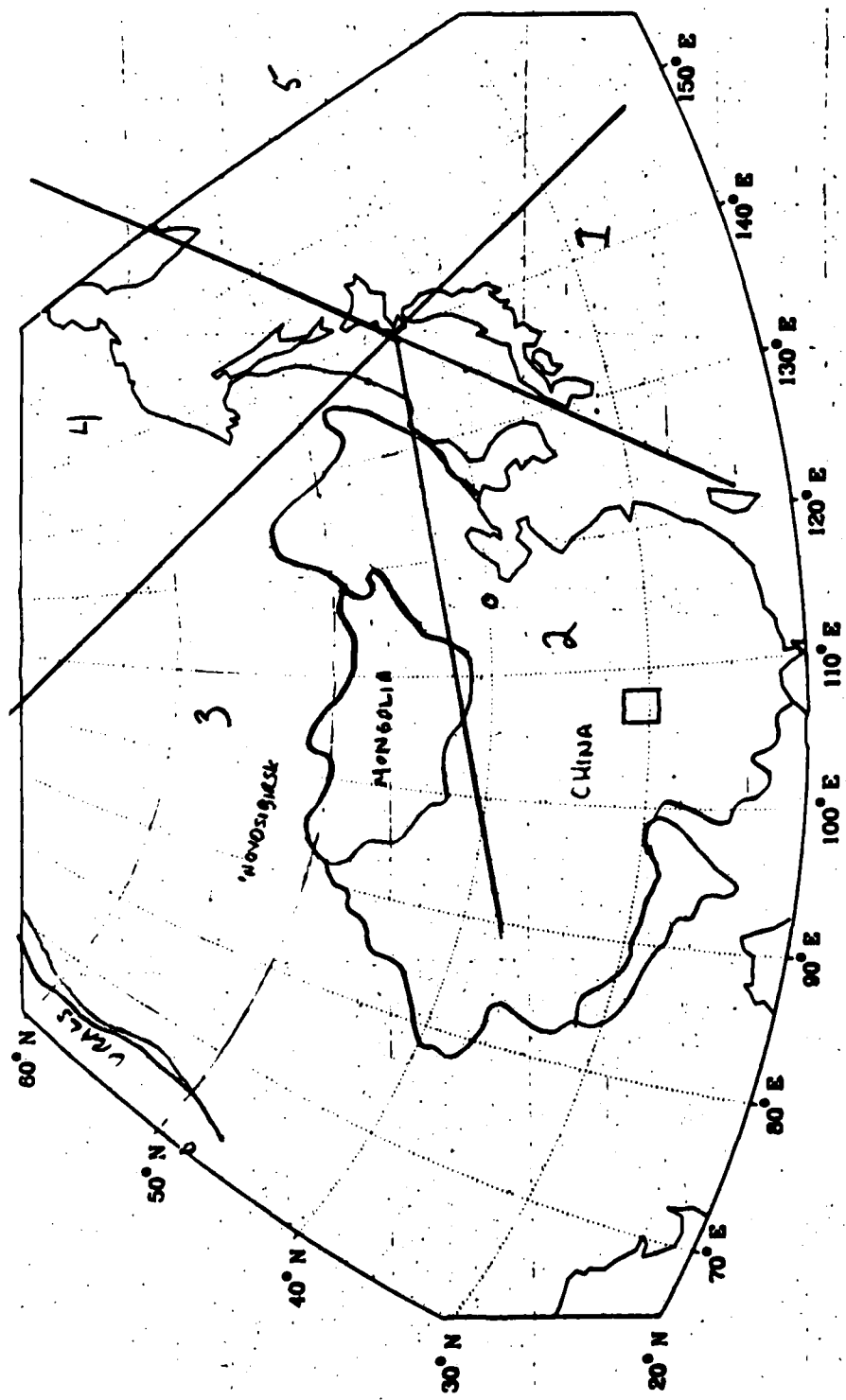
Figure 3.   Map of Eastern Asia, showing the five source sectors converging on Okushiri Island.

Table 9 shows the seven elemental signatures that we used to interpret the Okushiri Island samples, including earlier ones from the Central Soviet Union, China, and Europe, supplemented by the more-recent Northern China (Manchuria) and Japan signatures. Table 10 shows how the three principal elemental ratios varied by sector and season, as derived from categorizing each sample into the sector of its most representative 1000-mb trajectory (trajectories were supplied by Joyce Harris of NOAA/GMCC in Boulder). All three ratios decreased from winter to spring, indicating that the nearer sources (China and Japan), which have lower ratios, are relatively more important than the more-distant Soviet Union during the warm season. Interestingly, however, the absolute concentrations of aerosol from the Central Soviet Union were as high at Okushiri Island during spring as during winter, even though winds were weaker from the west.

Figure 4 shows the strongest pulse of aerosol from industrialized Manchuria, by means of six daily maps of trajectories with elemental concentrations, ratios, and apportionments superimposed. Beginning on 26 November 1984, the aerosol was a mixture of Asian sources, with none dominating. On the 27th, as trajectories began to dip southward toward Manchuria, the regional coefficient of NCHINA (Manchuria) rose from 0.04 to 0.21. On 29 and 30 November, coefficients of NCHINA reached their maximum values of the entire six-month experiment (4.2 and 2.9). By 1 December, in response to the trajectories dipping farther south, the NCHINA coefficient had declined to 0.54. The NCHINA signature was derived by averaging the samples of the 29th and 30th.

Figure 5 is another series of six maps which show Central Soviet Union aerosol giving way to recycled Arctic aerosol at Okushiri Island. During the first three days (2-4 January 1985), air came to Okushiri Island from the direction of the Central Soviet Union, and the CUSSR signature predominated. On 5 January, however, the trajectories veered northward and brought Arctic aerosol to Okushiri Island for a few days, the first three of which are shown here. The coefficients of the Central Soviet Union decreased by factors of 3-5, and European-like aerosol was required to explain the composition of these samples. We propose that this mixture of CUSSR and EUR is nothing more than Arctic haze being observed farther south than ever before.

Table 11 shows how the CUSSR signature is needed to account for elemental abundances in four typical samples with trajectories from the Central Soviet Union. Results for three combinations of signatures are shown: CUSSR-CHINA, CUSSR-CHINA-NCHINA, and CHINA-NCHINA. Note that the first two combinations explain all the elements well but that the third combination, without CUSSR, severely underestimates noncrustal V and overestimates Sb and Se.

Table 12 shows the equivalent calculation for the average Okushiri Island aerosol. Again, CUSSR is required to fit the elemental data properly. Tables 11 and 12 together constitute our strongest evidence for detecting Central Soviet Union aerosol at Okushiri Island, i.e., that the experiment succeeded.

41

Table 9. Elemental signatures used to apportion aerosol at Okushiri Island

	CUSSR	CHINA[1]	CHINA[2]	NCHINA[3]	JAPAN[4]	JAPAN[5]	EUR
As	10.0	3.8	2.9	10.7	1.28	1.6	3.7
Sb	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Se	1.03	1.53	1.92	0.25	0.24	0.34	2.2
Noncr. V	6.5	1.82	0.48	0.32	1.33	2.5	11.6
Zn	45	69	77	14.8	35	70	106
Noncr. Mn	4.4	6.3	9.3	1.72	4.3	2.8	5.4

[1] Six samples from Beijing-Tianjin and 13 from southwestern China
[2] Beijing-Tianjin samples only
[3] Two samples with extremely high As
[4] Monthly averages from 16 sites in Japan
[5] Monthly averages from Sapporo and Nappora only

Table 10. Elemental ratios in samples segregated by sector and by season.

Winter (25 Nov. 1984 - 28 Feb. 1985)

	1(N=0)	2(N=4)	3(N=50)	4(N=13)	5(N=11)	?(N=7)
As/Sb	-	7.0±2.6	8.5±3.9	8.7±6.0	5.4±3.3	7.2±2.9
Se/Sb	-	0.91±0.47	0.87±0.40	1.24±0.92	1.84±1.98	0.83±0.40
Noncr.V/Sb	-	2.8±1.1	4.0±2.2	4.8±3.4	3.2±4.0	4.2±2.7

Spring (1 March - 31 May 1985)

	1(N=8)	2(N=10)	3(N=32)	4(N=2)	5(N=4)	?(N=35)
As/Sb	4.2±1.1	5.7±1.1	5.9±3.7	4.7±3.7	4.0±1.4	4.4±2.6
Se/Sb	0.74±0.18	0.52±0.22	0.92±0.80	1.16±0.57	0.57±0.28	0.83±0.55
Noncr.V/Sb	2.2±1.0	2.0±1.2	3.1±2.4	3.4±1.8	1.73±0.51	3.1±2.4

43
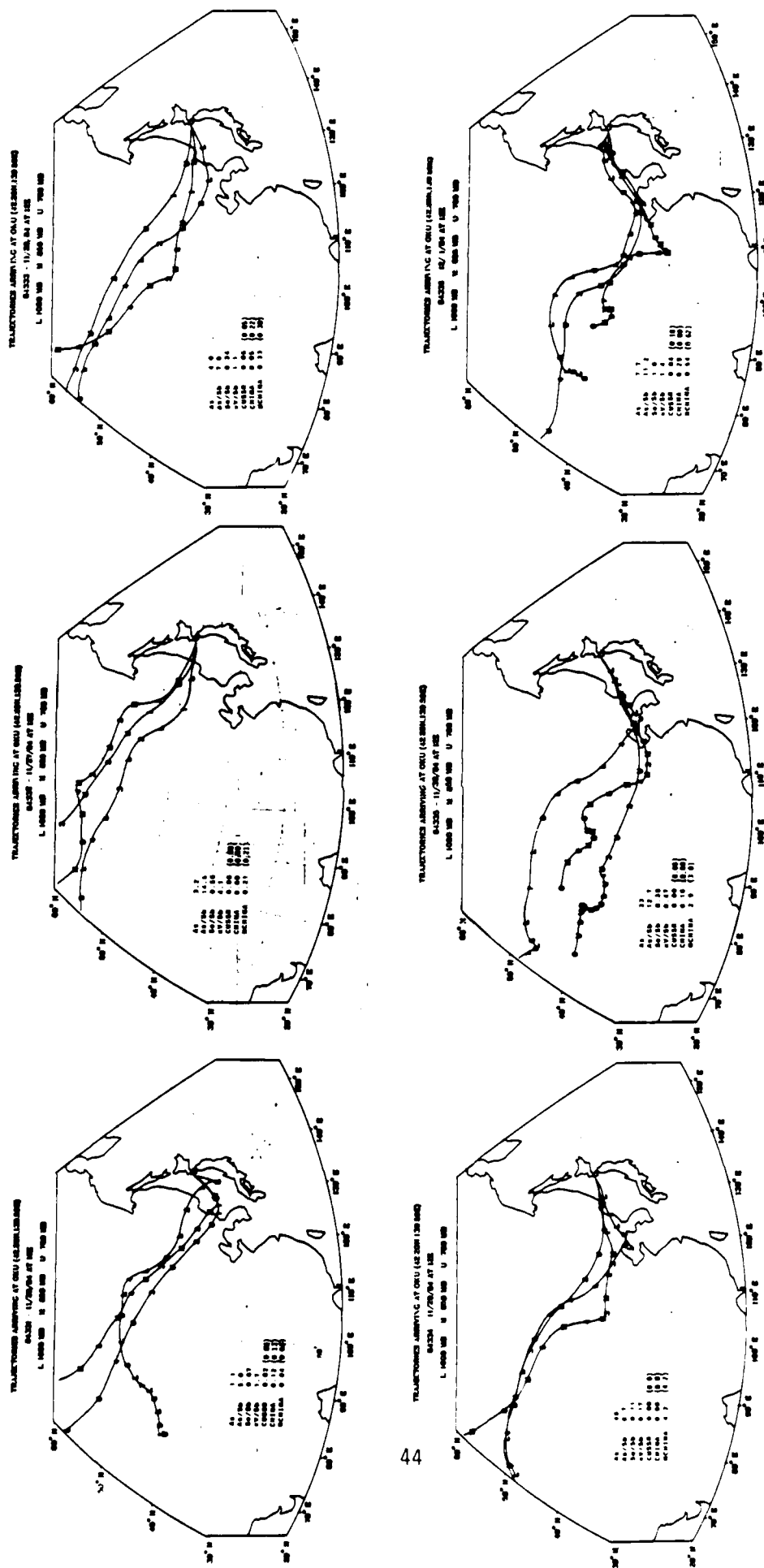
Figure 4. Trajectories, elemental concentrations, and elemental ratios for an episode of aerosol from industrialized Manchuria.
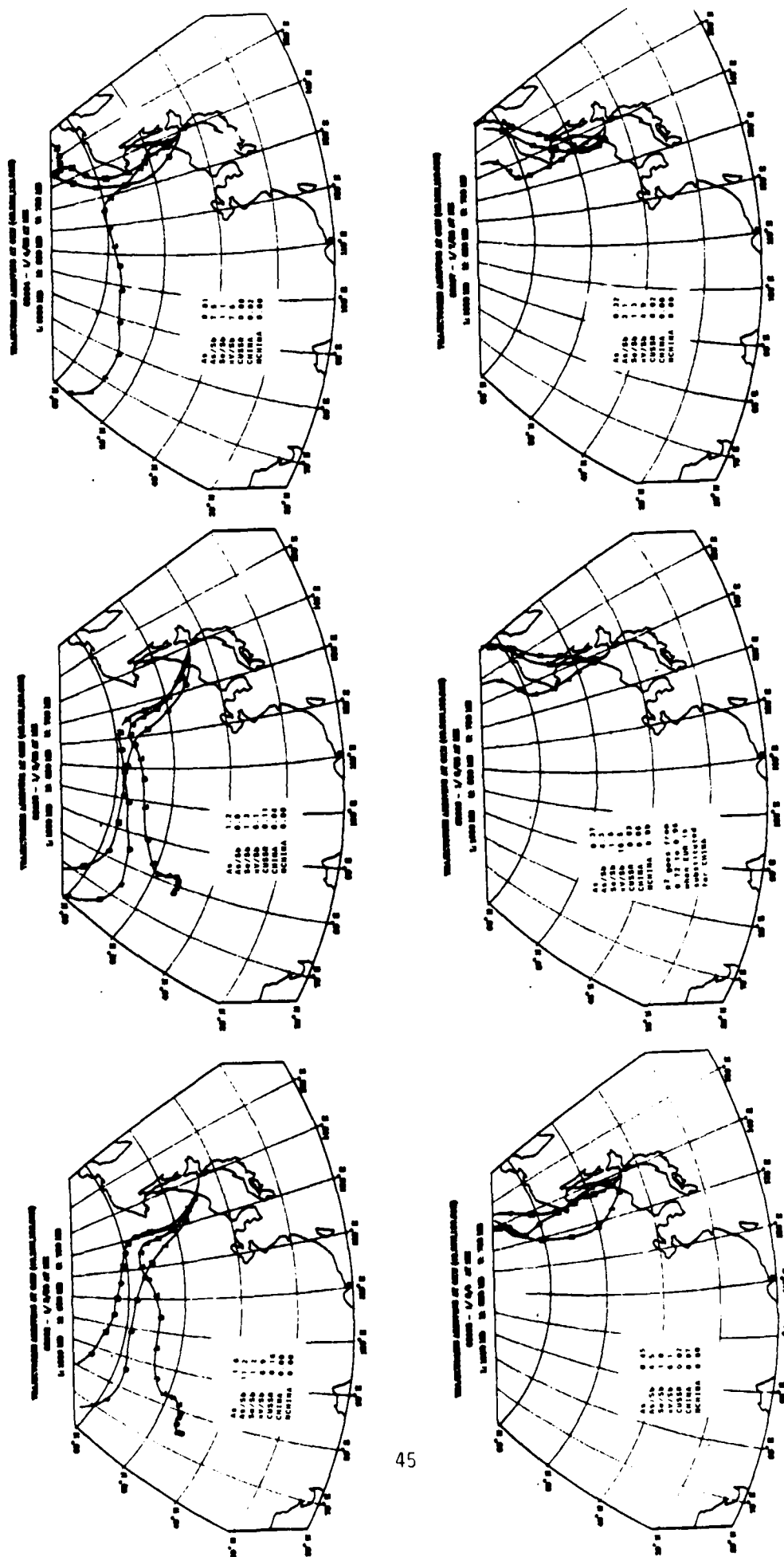
Figure 5. Trajectories, elemental concentrations, and elemental ratios for a period of aerosol from the Central Soviet Union giving way to a period of Arctic aerosol at Okushiri Island.

<u>Table 11. Fits of regional apportionments to four samples from the
CUSSR sector with various combinations of signatures</u>

	Actual	Predicted		
		<u>CUSSR,CHINA</u>	<u>CUSSR,CHINA,NCHINA</u>	<u>CHINA,NCHINA</u>

<u>1 January 1985</u>

	Actual	CUSSR,CHINA	CUSSR,CHINA,NCHINA	CHINA,NCHINA
As	1.38	1.39	1.39	1.33
Sb	0.16	0.15	0.15	0.18
Se	0.16	0.17	0.17	0.16
Noncr.V	0.92	0.89	0.87	0.19

<u>2 January 1985</u>

	Actual	CUSSR,CHINA	CUSSR,CHINA,NCHINA	CHINA,NCHINA
As	1.64	1.61	1.61	1.49
Sb	0.15	0.16	0.16	0.26
Se	0.18	0.17	0.16	0.31
Noncr.V	1.01	1.05	1.03	0.37

<u>3 January 1985</u>

	Actual	CUSSR,CHINA	CUSSR,CHINA,NCHINA	CHINA,NCHINA
As	1.24	1.25	1.25	1.15
Sb	0.14	0.15	0.15	0.22
Se	0.19	0.17	0.17	0.28
Noncr.V	0.85	0.79	0.79	0.33

<u>4 January 1985</u>

	Actual	CUSSR,CHINA	CUSSR,CHINA,NCHINA	CHINA,NCHINA
As	0.81	0.91	0.91	0.73
Sb	0.11	0.10	0.10	0.18
Se	0.12	0.12	0.12	0.27
Noncr.V	0.82	0.59	0.59	0.32

Table 12. Fits of regional apportionments to 95 samples at Okushiri with various combinations of signatures

	Actual	Predicted					
		CUSSR CHINA[1] NCHINA	CUSSR CHINA[2] NCHINA	CUSSR CHINA[1] JAPAN[3]	CHINA[1] JAPAN[3] NCHINA	CUSSR JAPAN[3] NCHINA	CUSSR JAPAN[4] NCHINA
As	3.1	3.1	3.1	2.9	2.9	3.1	3.1
Sb	0.37	0.35	0.35	0.39	_0.47_	0.39	0.39
Se	0.24	0.28	0.29	_0.35_	0.30	0.19	0.19
Noncr.V	0.94	0.82	0.78	_1.89_	_0.47_	0.96	0.96

[1] Beijing-Tianjin and Southwest China
[2] Beijing-Tianjin only
[3] 16 sites in Japan
[4] Sapporo and Nappora only

31. Third Symposium on Arctic Air Chemistry, Toronto, May 1984

The Third Symposium on Arctic Air Chemistry was held at the Atmospheric Environment Service in Toronto 7-9 May 1984. It was hosted by L.A. Barrie of AER and chaired by K. Rahn. In total, 31 papers were presented there, on topics including:

- North American, Greenland, and Norwegian sectors of the Arctic
- Chemical, physical, and radiative properties of the aerosol
- Gaseous and particulate pollutants
- Surface and aircraft measurements
- Meteorological aspects of Arctic air pollution
- The history of Arctic haze.

32. Arctic issue of ATMOSPHERIC ENVIRONMENT, December 1985, K. Rahn Guest Editor

The December 1985 issue of Atmospheric Environment, entitled "Arctic Air Chemistry", was devoted to 15 papers from the Third Symposium on Arctic Air Chemistry and eight papers on closely related topics. K. Rahn served as Guest Editor.

33. International Symposium on Arctic Atmospheric Pollution, Cambridge, England, September 1985

The State of Alaska sponsored the International Symposium on Arctic Atmospheric Pollution at the Scott Polar Research Institute, Cambridge, England, 2-5 September 1985. K. Rahn attended and presented a paper written with D.H. Lowenthal entitled "Who's polluting the Arctic? Why is it so important to know? An American perspective." This paper described URI's regional elemental tracer system and how it has been applied to determining sources of Arctic haze during winter 1979-80 and during the AGASP I experiment of March-April 1983. As noted above, the new WUSSR and CHINA signatures were presented there for the first time. K. Rahn also served on the planning committee for the symposium.

MISCELLANEOUS

34. Discovery of Sahara dust over Rhode Island

We have been interested in long-range transport of desert dust since the mid-1970's, when K. Rahn became involved with Sahara dust through the Max-Planck-Institut für Chemie in Mainz, West Germany. One of the first results of our Arctic Haze Contract was to find a major pulse of Asian desert dust reaching Barrow, Alaska in late spring 1976. After that, desert dust receded in importance to us as pollution aerosol was found to be the dominant contributor to Arctic haze.

In July 1984, however, we accidentally discovered an episode of Sahara dust in Narragansett, Rhode Island, the farthest north that it has ever been found. During the weekend of 21-22 July 1984, we noticed that the atmosphere was unusual: it was hot and humid but not hazy. Normally, hot and humid weather at Narragansett is also hazy, because the heat and humidity are picked up as air masses are transported long distances from the Gulf States, during which time they also accumulate large quantities of pollutants which combine with the humidity to create the haze. We noted the absence of haze on the 22nd but didn't think anything more about it.

The filter changed the next morning was distinctly yellowish-brown, as opposed to the normal gray. At that point, the Sahara explanation came to mind immediately. Proving it was much harder, however, because it is inherently improbable.

A quick scan of earlier filters showed that the one from the previous day was also brownish, but that no other filters that summer were. Thus, aerosol from the 21st and 22nd had to be explained. The weather maps from the local newspaper revealed that air of these two days had indeed come to Rhode Island from straight to the south, i.e., had not directly contacted the East Coast. Before then it had probably come from the east, as it was associated with the Bermuda high. When our German meteorological maps arrived a few days later, they confirmed this conclusion, and made it quite probable that air of 21-22 July 1984 had come from Africa.

We then had to see whether the soil dust could merely have been of local origin. We examined the filters under an optical microscope and determined that the soil particles were very small, most under 1 μm radius. This meant that they were highly aged (transported several thousand km or more) and also could not have been derived from nearby sources. Furthermore, their color was inconsistent with local sources: they were light yellowish-brown whereas local soil is much deeper brown with no hint of yellow. The last test of local vs. distant origin was to compare the elemental composition of local soil with the soil on the filters. We are presently analyzing local soil; so far, nothing unusual features have shown up, and we expect this test not to be definitive. Thus, of three tests of soil dust, two point to distant sources and one is neutral.

We analyzed the filters from 12 July through 1 August 1984 elementally. The results confirmed our visual impressions: on the 21st and 22nd, soil elements such as Al, Fe, and Sc were unusually concentrated while pollution elements such as As, Se, Sb, and sulfate reached exceptionally low levels for summer. This combination of high soil and low pollution had never been seen before to such an extreme. The yellowish-brown of the filters was indeed soil, the near-absence of black carbon did indeed mean that pollution was minimal.

Subsequently, we received back-trajectories from Joyce Harris of NOAA/GMCC in Boulder, Colorado. They showed clearly that on the 21st and 22nd of July, but no other days of this period, the air did indeed come from the equatorial Atlantic, even to 18,000 ft. Thus, our original hypothesis on Sahara dust has been confirmed by several independent tests, and not denied by any tests. We

are presently finishing up some loose ends to this story, and will be submitting our findings for publication within the next months.

Is this episode of Sahara dust of interest to ONR, considering that it is neither in the Arctic nor directly related to the strong optical effects of smaller-sized pollution aerosol? The answer is clearly yes, for several reasons. First and foremost is that this little episode has served to remind us once more that large quantities of natural and pollution products are being transported routinely long distances through the atmosphere in ways and with frequencies that we still do not fully appreciate. With the sophisticated chemical and meteorological tools now available to atmospheric researchers, we sometimes lapse into thinking that we know pretty well what's going on up there. Then comes a pulse of dust quite unexpectedly to show us that we really don't know so much after all. How many things like Sahara dust are occurring around us all the time that we are still missing? The net effect on our group of discovering this Sahara dust has been to humble us and cause us to redouble our efforts to understand long-range transport of aerosol in the atmosphere.

35. Radioactivity from Chernobyl measured at Barrow, Alaska and Narragansett, Rhode Island

As soon as we heard that a power reactor in the Ukraine had exploded and was releasing large quantities of fission products into the atmosphere, we realized that we had just been provided with a unique opportunity for a direct tracer experiment. Our previous work had shown that both the Western and Central Soviet Union contribute measurable amounts of pollution aerosol to the Arctic atmosphere, via a variety of pathways which are now fairly well understood; the prospect of a direct tracer from the Western Soviet Union, with zero background, was too good to pass up.

It turned out that this effort consumed us for one month. We began by counting our daily aerosol samples from Narragansett for ambient radioactivity, i.e., before they were irradiated for trace-element purposes. This involved only a minor change in our procedures, for we could use the same gamma-counting equipment as for the trace elements. Each morning after we removed a filter from the sampler, we pressed half into a pellet, allowed the short-lived natural daughters of ^{222}Rn to decay during the day, and counted the pellet for 16 hours overnight. The next morning, the gamma spectrum was processed by computer to give the corrected concentrations of the various fission products.

One major unknown was the path that the radioactivity would follow on its way to the U.S. and the exact time it would first reach North America. We and others knew that a polar pathway was quite possible, in addition to the better-known midlatitude pathway controlled by the prevailing westerlies. To help address this question, we offered to NOAA to analyze daily filters from Barrow promptly if they would ship them by overnight express. Dr. L. Machta agreed, because we could provide results from Alaska faster than anyone else could, and we were soon receiving daily filters from Barrow. Of course, "overnight" is a loose term when applied to shipments from Arctic Alaska; 2-4 days was typical.

50

The reactor in Chernobyl exploded 25 April, East Coast time. The first radioactivity arrived in Narragansett 7 May, after it which rose rapidly to a maximum on 9-10 May. It then declined somewhat less rapidly, went nearly to zero, passed through a second smaller maximum about two weeks later, and continued to decrease slowly. Curiously, it arrived in Barrow one day later than in Narragansett, reached a much lower maximimum, declined, but then passed through a stronger second maximum than at Narragansett.

We did much more than simply monitoring concentrations, though. As it turned out, perhaps the most significant thing we did was to communicate the results regularly to interested parties in the state. The three television stations in Providence visited us regularly for basic explanations and updates; at one point, television crews were here four working days in succession. Every morning for a month, weekends included, we telephoned the previous day's results to the three TV stations and the Rhode Island Department of Health. This media exposure served a real purpose, for Rhode Islanders had no other source of data on the radioactivity surrounding them. The Department of Health sent samples of air, rain, and milk regularly to EPA in Montgomery, Alabama, but got no results back for at least the first month. Thus, we were literally the only source of data for Rhode Island.

We did not limit ourselves to monitoring air, however. Dr. Roy Heaton of our group measured the radioactivity in every rainfall, and we reported the results to the public along with the aerosol data. The Department of Health supplied us with regular milk samples, in which we detected small amounts of radioiodine. We also looked for radioactivity on shoes and handbags of travelers returing from Europe and the Soviet Union (and found it in abundance).

As time permits, the more technical results will be reported formally. In the meantime, we feel that we benefited greatly from the experience of observing direct transport from the Western Soviet Union to the northeastern United States. We were very impressed by how efficiently and rapidly the material moved, and how little its concentrations decreased as the cloud passed from one side of North America to the other. This experience showed us that we must be prepared to deal with more regional signatures simultaneously in our tracer system than we expected to, even to the point of involving different continents in apportionments. We see clearly now that aerosol from the Soviet Union routinely reaches the United States; we must ultimately deal with it whenever we deal with U.S. aerosol. That is a tall order, to be sure, but a worthy goal. This realization is one of the major reasons for the major effort to extend the tracer system being proposed for the next three years of work under ONR.

36. Tracer system being extended into stream water in search for effects of acid rain in Rhode Island (unfunded cooperation with Rhode Island College)

This work doesn't really have any direct connection with ONR and Arctic haze. We mention it briefly here because it shows how spinoffs can have spinoffs, and how important it is to fund initial work in a area which has the potential to breed others.

Our tracer system for aerosol has now led to a viable tracer system for pre-
cipitation, as explained earlier in this report. The tracer system for precipi-
tation has in turn allowed us to attempt to evaluate the extent to which acid
rain has changed the chemistry of Rhode Island's waterways, one of the most
important environmental issues in the state. We recently learned that the
available data on acidities and alkalinities of rivers and streams in Rhode
Island can be and have been interpreted in two opposite ways: severe degrada-
tion over one-half the state or no degradation at all. Historical data are not
available to resolve this controversy.

As a service to the State, we would like to use our analytical capabilities
to find out whether acid rain is damaging Rhode Island's streams. To begin, we
decided to compare the detailed elemental composition of Rhode Island rain (our
18 months of data from Narragansett generated under the DOE project) with ele-
mental composition of stream water. The data for streams are being generated
via an unfunded cooperative project with Prof. Kenneth Borst of Rhode Island
College, who has been sampling Rhode Island's waterways for three years and
measuring acidity and alkalinity in them. Prof. Borst has more data on the sub-
ject than anyone else in the State. Under our guidance, he is analyzing certain
streams for dissolved and particulate elements. To date only three streams have
been done, but they are sufficient to reveal certain regularities in composition
which we think will turn out to be important.

So aerosol work led to precipitation work led to stream work. Although the
stream project is still small, it may grow as well. Prof. Borst wants to
involve a colleague from Rhode Island College; we may be able to contribute a
graduate student to the project via supplementary funds from DOE.

37. Ideas on the fate of Arctic haze

What is the ultimate fate of Arctic haze? Some years ago, we estimated that
one-quarter to one-half would be deposited in the Arctic, and that the rest
would return to mid-latitudes. The fundamental reason that so much leaves the
Arctic is of course the unusually long residence times caused by stability of
the winter Arctic atmosphere, the smoothness of the surface, and the meager pre-
cipitation. The same long residence times which allow the haze to be
transported such long distances from midlatitudes also allow it to often escape
from the Arctic.

Because comparable amounts of Arctic haze should both leave the Arctic and
be deposited there, the correctness of these calculations could in principle be
verified in two ways: by directly observing the amount of Arctic aerosol depo-
sited in the Arctic snowpack as well as directly observing the amount of aerosol
leaving the Arctic. At present, there seem to be no elemental data for the
Arctic snowpack which could be used to calculate how much Arctic haze is depo-
sited there each winter. There are, however, some recent observations which
suggest that large amounts of Arctic haze may indeed be observed entering cer-
tain midlatitude regions during winter. While these data are highly preliminary
and still quite indirect, they do support the general idea that much Arctic haze
leaves the Arctic before being removed from the atmosphere.

The relevant observations are:

- Our data from Okushiri Island, which show a strong pulse of Arctic-like aerosol from due north in winter.
- Observations by the University of Washington (Dagmar Cronn and associates) of elevated concentrations of halocarbon gases near Pullman, Washington during winter immediately behind cold fronts (Carter et al., 1983). Halocarbons are known to be enriched in Arctic air masses (Khalil and Rasmussen, 1983; for example), and may be effective indicators of its presence when aerosol data are not available.
- Len Barrie's (AES, Canada) high sulfate and SO_2 in the Prairie Provinces during winter, even with "clean" air from the north.

Each of these observations can and should be followed up. Our plans for doing this are discussed in Section II of this report.

53

C. PUBLICATIONS RESULTING WHOLLY OR PARTLY FROM THIS PROJECT
AUGUST 1983 - JULY 1986

From August 1983 - July 1986, this project contributed wholly or in part to 20 publications, with three more in press:

                    JR = Journal article, refereed
                   JNR = Journal article, nonrefereed
                     P = Popular article
                    CH = Chapter of book
                    CP = Conference proceedings
                     R = Report

CP   Rey L., Ottar B, Rahn K.A. and Shaw G.E. (1983) Arctic environmental
      issues of energy production at mid-latitudes and the role of long
      distance air transport of pollutants. Proceedings of the 12th
      Congress of the World Energy Conference, New Delhi, 18-23 September
      1983.

CP   Rahn K.A. Lewis N.F. and Lowenthal D.H. (1983) Elemental tracers of
      Canadian smelter aerosol transported into the northeastern United
      States. pp. 163 ff. of Receptor Models Applied to Contemporary
      Pollution Problems, SP-48, Air Pollution Control Association,
      Pittsburgh, Pa.

JR   Berg W.W., Sperry P.D., Rahn K.A. and Gladney E.S. (1983) Atmospheric
      bromine in the Arctic. J. Geophys. Res., 88, 6719-6736.

JR   Prospero J.M., Charlson R.J., Mohnen V., Jaenicke R., Delany A.C.,
      Moyers J., Zoller W. and Rahn K. (1983) The atmospheric aerosol
      system: An overview. Rev. Geophys. Space Phys., 21, 1607-1629.

JNR   Rahn K.A. (1983) A reply to "KLW's" critical review. Environ. Forum 2,
      14-22.

JR   Rahn K.A., Lewis N.F., Lowenthal D.H. and Smith D.L. (1983) Noril'sk
      only a minor contributor to Arctic haze. Nature 306, 459-461.

CP   Rahn K.A. and Lowenthal D.H. (1983) The promise of elemental tracers
      as indicators of source areas of pollution aerosol in the eastern
      United States. pp. 189-197 of Trace Substances in Environmental
      Health - XVII, D.D. Hemphill, Ed., University of Missouri, Columbia.

JR   Rahn K.A. and Lowenthal D.H. (1984) Elemental tracers of distant
         regional pollution aerosols. <u>Science</u> <u>223</u>, 132-139.

P   Rahn K.A. (1984) Who's polluting the Arctic? <u>Natural</u> <u>History,</u> <u>93</u>, 30
         ff.

P   Rahn K.A. (1985) USSR's cooperation may provide a new piece in the
         Arctic Haze puzzle. <u>Maritimes</u> <u>29</u>(1), 1-3.

JR   Thurston G.D., Laird N.M., Rahn K.A. and Lowenthal D.H. (1985) Tracing
         aerosol pollution. <u>Science</u> <u>227</u>, 1406,1408,1412.

JR   Rahn K.A. and Lowenthal D.H. (1985) Pollution aerosol in the Northeast:
         northeastern-midwestern contributions. <u>Science</u> <u>228</u>, 275-284.

R   Lewis, N.F. (1985) Particle-size distributions of the Arctic aerosol.
         M.S. Thesis, University of Rhode Island, 124 pp.

JR   Rahn K.A. (1985) Progress in Arctic air chemistry, 1980-1984.
         <u>Atmos. Environ.</u> <u>19</u>, 1987-1994.

JR   Lowenthal D.H. and Rahn K.A. (1985) Regional sources of pollution aero-
         sol at Barrow, Alaska during winter 1979-80 as deduced from elemental
         tracers. <u>Atmos. Environ.</u> <u>19</u>, 2011-2024.

JR   Halter B.C., Harris J.M. and Rahn K.A. (1985) A study of winter variabi-
         lity in carbon dioxide and Arctic haze aerosols at Barrow, Alaska.
         <u>Atmos. Environ.</u> <u>19</u>, 2033-2037.

R   Rahn K.A., Wunschel K.R. and Lowenthal D.H. (1986) <u>Elemental tracers</u>
         <u>applied to transport of aerosol from Midwest to Northeast</u>. Report
         EPA/600/S3-86/015, May 1986, Atmospheric Sciences Research
         Laboratory, U.S. Environmental Protection Agency, Research Triangle
         Park, NC 27711 (available from NTIS).

R   Rahn K.A., Wunschel K.R. and Lowenthal D.H. (1986) <u>Project Summary,</u>
         <u>Elemental tracers applied to transport of aerosol from Midwest to</u>
         <u>Northeast</u>, Report EPA/600/S3-86/015, May 1986. Summary available
         from Center for Environmental Research Information, U.S.
         Environmental Protection Agency, Cincinnati, OH 45268.

      Lowenthal, D.H. (1986) Regional source apportionment and related statisti-
         cal topics. Ph.D. Thesis, University of Rhode Island, 173 pp.

P   Rahn K.A. and Lowenthal D.H. (1986) The acid rain whodunit. <u>Natural</u>
         <u>History</u> <u>95</u>(7), 62-65.

In press:

JR   Lowenthal D.H. and Rahn K.A. (1986) Comments on "A quantitative
      assessment of source contributions to inhalable particulate matter in
      metropolitan Boston", by George D. Thurston and John D. Spengler.
      Atmospheric Environment.

CP   Rahn K.A. and Lowenthal D.H. (1986) Who's polluting the Arctic? Why is it
      so important to know? An American perspective. Proceedings of the
      International Symposium on Arctic Atmospheric Pollution, 2-5
      September 1985, Scott Polar Research Institute, Cambridge, England.

JR   Lowenthal D.H., Hanumara R.C., Rahn K.A. and Currie L.A. (1986) Effects
      of systematic error, estimates and uncertainties in chemical mass
      balance apportionments: Quail Roost II revisited. Atmospheric
      Environment.

II. RENEWAL PROPOSAL: 1 October 1986 - 30 September 1989

A. INTRODUCTION AND RATIONALE

The last three years of our Arctic Haze Contract have been very productive. As described in detail above, we formalized the regional elemental tracer system, developed signatures for it from three continents, publicized it, saw it officially approved by EPA, and applied it to Arctic haze.

Neither the tracer system nor our understanding of Arctic haze is complete yet, however. For every advance, new questions and opportunities have arisen. During the next three years, we plan to build on and extend the accomplishments of the past three years via a program of continued research on Arctic haze which addresses some of these new topics. We will emphasize strengthening our elemental tracer system, attempting to determine the history of Arctic haze by analyzing the Russian/Norwegian ice core from Nordauslandet, analyzing aircraft samples from the AGASP II experiment of spring 1986, analyzing a rare summer haze event from Alaska in 1986, and looking into the fate of Arctic haze.

- The tracer system will be improved in at least four ways: its statistical aspects will be refined, innovative ways of deriving signatures from hard-to-sample areas will be explored, and the tracer power of up to 15 additional elements will be determined.

- From the Nordauslandet core, as many as 100-200 samples of ice will be analyzed for trace elements with our new technique developed under DOE sponsorship. We hope to use the results to write both the modern history of Arctic haze and the history of the various regions contributing to it.

- An extensive set of aircraft samples from AGASP II will be analyzed for trace elements and compared with the results of other investigators. (Dr. Lowenthal has already begun this work.)

- A strong haze event which covered much of Alaska during late July and early August 1986 will be studied by means of our filter samples from Barrow as well as others provided by Dr. Glenn E. Shaw of the University of Alaska. After understanding this event, we will use our library of filters from Barrow and Fairbanks to examine whether summer haze is a regular feature of the Arctic. Filters to be analyzed will be selected both meteorologically and from NOAA/GMCC's records of light scattering at Barrow.

- The fate of Arctic haze will be approached in two different ways: snowpack from Barrow and northern Canada (if possible) will be analyzed for trace elements and the deposition of Arctic haze within the Arctic calculated; from aerosol samples taken along principal pathways out of the Arctic, the net loss of Arctic haze during winter will be estimated. Eventually, we will work with Dr. Randolph Borys in collecting snow at Barrow directly and analyzing it chemically.

57

In addition, we will assist Dr. B. Ottar of the Norwegian Institute for Air Research in planning for the Fourth Symposium on Arctic Air Chemistry, to be held in Oslo in September 1987.

These major projects, as well as some minor ones, are discussed individually below.

B. SPECIFIC PROJECTS

1. Sampling and analysis of Barrow surface aerosol

With the cooperation of the staff at NOAA/GMCC's baseline observatory in Barrow, Alaska, we will continue to have continuous aerosol samples taken for us there. As in recent years, selected periods of samples will be analyzed. We now have 10 years of samples from Barrow, which form a very valuable archive.

2. Statistical refinements to elemental tracer system

Even though Dr. Lowenthal has completed his Ph.D. thesis on statistical aspects of our elemental tracer system, the subject itself needs to be pursued further. During the next three years, we intend to devote roughly 20% of our efforts under this ONR Contract to following up selected statistical topics, including:

- Using factor analysis and/or cluster analysis to deduce the major elemental signatures in large suites of aerosol samples. It is extremely important to understand whether objective statistical approaches such as factor analysis and cluster analysis can really be used to derive regional signatures reliably. There is currently a serious debate within the field of receptor modeling concerning whether factor analysis is ever reliable; we believe that it can be useful under certain circumstances, and have just submitted a paper to that effect to Atmospheric Environment (Lowenthal and Rahn, 1986). We wish to participate meaningfully in this continuing debate, for we sense that current feelings are swinging too far against factor analysis.

- Deriving a meaningful measure of the degree of collinearity among regional signatures and its effect on regional apportionments. Everybody talks about collinearity; few do anything about it. We have two fully operational ways of evaluating collinearity in signatures, but still do not understand collinearity or the objective tests of it to our satisfaction (no one else seems to, either). Using our large data bases, our collection of regional signatures, and Dr. Lowenthal's ability to manipulate both on our PRIME 550 computer, we will attempt to gain a better appreciation of the real degree of degradation of our apportionments introduced by collinearities among signatures. Out of this, we hope to gain further guidance concerning the number of signatures we can handle simultaneously, as a function of the number of additional elements in the tracer system.

58

- Understanding the true uncertainties in regional apportionments. We pre-
sently report an uncertainty with every regional coefficient; even though
these uncertainties are calculated with accepted statistical procedures,
we are not yet confident that they are realistic. (No one else in recep-
tor modeling of aerosols calculates uncertainties as rigorously as we do,
or attempts to understand their true meaning). We feel that conventional
mathematical methods may not be relevant to our particular needs, and wish
to look into this problem further.

- Better understanding the strengths and limitations of our multiple-linear-
regression method for apportioning sulfate or other nontracer species to
various source regions. As sulfate is the major component of fine-
particle aerosol, and associated with the majority of the acidity in pre-
cipitation, it is crucial that we understand the limits of our
apportionments. At face value, apportioning sulfate, whose proportions to
tracer elements increase monotonically as an air mass ages and SO_2 is oxi-
dized, would seem to be folly. But we have a great deal of evidence that
the apportionments are actually nearly as reliable as those of the tracer
elements themselves. During the next three years, Dr. Lowenthal will
probe more deeply into this topic.

3. Innovative ways to derive elemental signatures of hard-to-sample regions

As discussed in Section I.B.10 above, we have begun to evaluate the feasibi-
lity of determining regional elemental signatures of aerosol from deposition on
plants, auto air filters, and swipes of deposition on windows. During the next
three years, we intend to devote roughly 20-25% of our total ONR effort to
pursuing this topic. The more that elemental tracing becomes accepted practice,
the more important it will be to have alternate ways of determining regional
signatures.

- We will give lichens the most attention in the near future, because they
look very promising. A graduate student in the Botany Department of URI, who is
studying lichens of western Rhode Island, has already provided us with samples
from there. Dr. Lowenthal has begun to analyze them, washed and unwashed, for
trace elements. The site where the lichens were collected, at the University's
W. Alton Jones Campus, is near enough to Narragansett that elemental data from
the lichens can be justifiably compared with our data for aerosol and rain taken
at Narragansett. We look upon these first analyses as an introductory exercise
only, and will later refine our procedures with a second round of samples taken
closer to Narragansett.

- Depending on the results of the experiment with lichens, local mosses may
be tried as well.

- After the lichens, we will return to the swipe experiment (where material
deposited on windows is rubbed onto a filter and analyzed) from New York City.
It will be duplicated and expanded, and tried in Narragansett as well.
Alternate surfaces will also be examined.

- We will follow up on our preliminary study of a Japanese automotive air filter by analyzing one or more American auto filters, in the hope that they are made from a material which contains less Sb than the Japanese filter did. If a satisfactory American filter can be found, a number of exposed filters will be analyzed for trace elements, and the results compared to Narragansett aerosol.

4. Noble metals as potential tracers.

As noted above in the Progress Report, we have just taken on Mr. David Elroi for M.S. research into the possibility of using noble metals in our tracer system. The 6-7 noble metals which can probably be measured in aerosols by neutron activation coupled with post-irradiation chemical separations represent potentially powerful tracers about which virtually nothing is known in aerosol. As an example of their potential importance, consider that Pt and Pd are used heavily for automotive catalysts in North America but not in Europe; if these elements are lost from catalytic converters to the atmosphere, as seems to be the case, North American aerosol might be substantially enriched in them relative to European aerosol. In the best of worlds, Pt and Pd might significantly improve our ability to distinguish North American from European aerosols chemically, and thereby refine our understanding of sources of Arctic haze correspondingly.

Mr. Elroi is in the process of assembling the equipment and chemicals necessary to measure noble metals in aerosols with radiochemical separations. Within about six months, we should know which can be measured reliably in rural and remote samples.

Later this fall, we plan to propose a three-year project on this work to NSF, having had indications from them that it would be acceptable. If the project is funded, we will transfer Mr. Elroi to it and take on another student under ONR.

5. Additional tracer elements by atomic absorption

As noted in the Progress Report, a recent survey of the periodic table suggested that nine elements determinable by atomic absorption might be suitable additions to our tracer system (Pb, Cd, Mo, Ag, Sn, Tl, Te, Bi, Be). To verify this, Mr. Andrew Hudson spent some time this past summer trying to measure them in typical aerosol samples. The work is not completed, and he plans to continue it part-time during the next year or so. To date, he has been able to measure the first six of these elements adequately. We think that atomic absorption definitely has a future as part of our tracer system, and would very much like to make it a permanent part of our operation. Unfortunately, it demands too large a commitment of time and funds to be supported fully under this ONR Contract. Mr. Hudson's study is a feasibility test only.

We have provided Mr. Hudson with several samples representing each of our major regional signatures. He will attempt to measure each of the nine elements in each sample, then we will combine the resulting data with our earlier neutron-activation results and see how much additional tracer power is offered

by the new elements. The next step, which may be too big to be supported here, is to check out the best of the new elements in practice by analyzing larger suites of receptor samples for them.

6. Analysis of Russian ice core from Nordauslandet

This will be one of our major efforts during the next three years. After Dr. Robert Delmas and associates of the Laboratoire de Glaciologie du CNRS in Grenoble, France have cleaned and sectioned the Russian ice core from Nordauslandet, K. Rahn will visit them and discuss which portions will be transferred to Rhode Island and how. The sections will presumably be shipped frozen, freeze-dried here, and then analyzed for trace elements by the same neutron-activation procedures currently used for rain and snow. Dr. Lowenthal is prepared to analyze 100-200 samples. We are very much looking forward to this project.

7. Analysis of aerosol samples from AGASP II

We have received a suite of 40 filter samples from the flights of AGASP II. Dr. Lowenthal has already finished analyzing them for trace elements and sulfate. He attended the first workshop on AGASP II, held at Fenelon Falls, Ontario, 8-10 October 1986, and discussed the results there.

An interesting controversy has arisen within AGASP II which we may be able to help resolve. In spite of the major eruption of Mt. St. Augustine whose plume of ash closed Anchorage International Airport and delayed the start of AGASP II, most AGASP investigators feel that the plume did not affect their subsequent measurements in the high Arctic. On the first flight a major polluted layer was intercepted, however, and its origin forms one of the most significant questions currently being addressed by AGASP. Dr. Glenn E. Shaw of the Geophysical Institute in Fairbanks feels very strongly that the Augustine plume must have reached the high Arctic, for he clearly saw it pass over Fairbanks moving northward.

We may be able to decide the Augustine question elementally. Dr. Shaw has filter samples from the Fairbanks area during the time the plume passed by, and will supply portions of them to us. We will analyze them by our usual neutron-activation procedures. If the plume turns out to be sufficiently intense, we may be able to derive a signature for it which could be used to see whether Augustine aerosol was found in any AGASP II filters from the high Arctic.

8. Summer haze in Alaska

As described in Section I.B.18 above, there was a major haze event over much of Alaska during July 1986. We have now generated considerable evidence that the principal haze aerosol was industrial, from greater Europe. In the course of analyzing this event, we were reminded that the literature shows that pulses of aerosol reach Barrow during most July's and August's, but have been ignored until now. We have ten years of summer filters from Barrow in our archives, and intend to analyze them selectively to try to document whether Arctic haze is a

61

regular, though infrequent, feature of the summer environment. If so, this would open up a whole new aspect of Arctic haze, and make it a more general phenomenon than previously considered. It should also make it easier to identify the meteorological conditions which effectively transport the haze, for they should stand out clearly from those of most of the summer when there is no haze in Alaska.

9. Field study of aerosol in the Soviet Union

As noted above in the Progress Report, we have been trying for the last several years to initiate a joint study of Soviet Union aerosol with our colleagues there, via Working Group VIII of the US-USSR Bilateral Agreement on Cooperation in the Field of Environmental Protection. After numerous meetings, K. Rahn visited the USSR in April 1984 to discuss plans for the project, which the USSR side eventually slowed down to the point that nothing has happened.

Now the USSR has requested that the project, which they still insist remains approved in principle, be shifted to the newly revived Working Group I, Air Pollution Modeling, Instrumentation and Measurement Methodology (we used Working Group VIII, on climate, earlier because it was the only one functioning at that time). Viewed dispassionately, the USSR request seems reasonable, because long-range transport fits better under modeling and instrumentation than under climate. We are concerned, however, that shifting working groups will delay the project even further. K. Rahn was invited to attend the next joint meeting of Working Group I in Washington 29 September 1986, and was given 90 minutes to discuss the joint project, but at the last minute the USSR side postponed the meeting until March or April 1987. We are disappointed by this latest delay, of course, but remain optimistic that the joint experiment will finally get under way.

In our view, a joint field experiment in the Soviet Union could provide extremely important data on regional signatures of USSR aerosol, something which until now has had to be inferred from measurements outside their borders. Both the Western and Central Soviet Union seem to emit aerosols with distinctive compositions which can be detected well downwind.

10. Continued cooperation with China

During the next years, we wish to continue to cooperate with Dr. Zhao Dianwu of the Institute of Environmental Chemistry in Beijing. Dr. Zhao is very interested in our elemental tracer technique as well as our studies in acid rain, and would like to have cooperative programs on both within China. He has already provided us with aerosol samples from the Beijing-Tianjin area of northern China and the Chengdu-Chongqing-Guiyang area of southwestern China. From these samples, we have been able to develop a preliminary signature of Chinese pollution aerosol.

The link to Dr. Zhao is too good to let die. As opposed to our colleagues in the Soviet Union who aren't familiar with western scientific literature and who have very little freedom to initiate projects, Zhao is aggressively soli-

62

citing our help, and offers concrete samples, projects, and general cooperation in return. Because China is so big and pollutes so much, because it may also be a source of Arctic haze, and because it borders the Soviet Union, we wish to continue to cooperate with Dr. Zhao.

Zhao has offered an exchange program as a next step in our relationship. Two of us will visit China for two weeks, probably in spring 1987, with all expenses within China provided by the Environmental Protection Office in Guiyang. In return, two scientists from Guiyang will visit the U.S. for two weeks, with URI providing their expenses within the U.S. In view of the great benefits which can come to our tracer program from this arrangement, we are requesting funds for this in the first year's budget here.

11. Eastern European signatures via Polish visitor

For years, we have wanted to have Dr. Urszula Tomza of the Institute of Physics, University of Silesia, Poland, work in our laboratory. Dr. Tomza has become very interested in air pollution in Poland and has spent several research visits at the Institute of Nuclear Sciences, University of Ghent, Belgium, measuring the elemental composition of pollution aerosol from Katowice. She is a tireless worker, and entirely dedicated to her subject.

One year ago, we learned that the Kosciuszko Foundation in New York sponsors exchange visits of Polish scientists to American laboratories. Dr. Tomza has applied for a one-year visit with us, beginning in Fall 1987. If she is accepted, we will use the time to increase our understanding of pollution aerosol emitted in Eastern Europe. The Eastern European signature is very important to us, not necessarily because Eastern Europe contributes largely to Arctic haze, but because the signature resembles that of the Central Soviet Union and can be confused with it if one is not careful.

With a bit of luck, then, our ONR Arctic haze project will benefit from Dr. Tomza's presence without sustaining any direct costs.

12. Experiments on fate of Arctic haze

Section I.B.37 of the Progress Report described observations from Okushiri Island (by us), Washington State (Dagmar Cronn et al.), and central Canada (Len Barrie of AES) which jointly suggest that pulses of Arctic haze reach midlatitudes fairly frequently during winter. We would like to use our elemental technique to pursue this topic. If Arctic outbreaks indeed bring Arctic haze to midlatitudes, measurements of frequency and intensity should allow us to place some bounds on the amount of haze which leaves the Arctic each winter. This in turn would place bounds on the amount of haze deposited in the Arctic, which is any important parameter from several points of view.

Currently, nothing is known about haze outbreaks in midlatitudes, so any knowledge gained would be important. We can think of at least four different ways to generate more information, all of which we will pursue:
(1) Dig more deeply into the preliminary indications from our Okushiri Island data to the effect that Arctic-like aerosol comes down from the north

during winter. By using refined air-mass trajectories and statistical tests, we will check the accuracy of this first observation.

(2) Dagmar Cronn and associates at Washington State University may be able to take filter samples for us at Pullman, Washington this winter or next to see whether the Arctic outbreaks which bring elevated concentrations of halocarbons (gaseous Arctic haze) also being particulate haze. K. Rahn will discuss this opportunity with her on a trip to the Pacific Northwest during November 1986.

(3) Dr. Len Barrie of the Canadian Atmospheric Environment Service in Toronto has discussed the fate of Arctic haze with K. Rahn several times. Barrie has generated data which suggest that mid-Canadian background concentrations of SO_2 and sulfate are higher in winter than in summer, the opposite of what one might expect if transport from the south were important. He has suggested that the elevated backgrounds might actually be from Arctic haze. We would like to check this elementally in a joint experiment, with the site(s) yet to be determined.

(4) A five-year set of filters taken every third day at St. Margaret's Bay, outside Halifax, Nova Scotia, is available to us courtesy of Dr. Rod Shaw, also of AES Canada. Until recently, we had thought of these filters in terms of their potential to reveal transport of pollutants from the United States to Nova Scotia, but now we realize that they may also be used to sense Arctic haze exiting through eastern Canada, which we believe to be one of the major pathways. To keep this effort reasonable, we propose to get a list of the dates of these samples and analyze only those on which the air is coming strongly from the Arctic.

13. Cooperation with NOAA - trajectory analysis by Joyce Harris

Dr. Jim Peterson, director of NOAA's Geophysical Monitoring for Climatic Change program in Boulder, Colorado, has repeatedly stated his desire to interact with us in ways more substantial than just collecting filters in Barrow. This cooperation has most recently taken the form of a joint article on CO_2 and pollution aerosol at Barrow (Halter et al., 1985), as well as air-mass trajectories for Okushiri Island and Narragansett supplied by Joyce Harris.

During the next three years, we will continue to receive trajectories from Mrs. Harris on a number of projects of interest to NOAA. Isentropic trajectories should be calculated both for Okushiri Island and Narragansett, to be compared with the isobaric ones we already have. A bit more in the future, we will probably need trajectories for the summer 1986 haze event in Alaska which may have originated in Europe and the Western Soviet Union.

14. Fourth Symposium on Arctic Air Chemistry

The Fourth Symposium on Arctic Air Chemistry is currently scheduled to be held at the Norwegian Institute for Air Research, Lillestrom, in September 1987. Dr. B. Ottar, director of the institute, will be chairman and host. K. Rahn will assist in planning the symposium, as he has hosted or chaired the earlier three in the series.

64

C. FACILITIES AVAILABLE

Most of the work proposed here will be done in the Rhode Island Nuclear Science Center (RINSC), where the URI Graduate School of Oceanography's Center for Atmospheric Chemistry Studies Tracer/Arctic Section (our group) is located. The RINSC swimming-pool reactor operates at two megawatts seven hour per day, five days per week, and delivers a thermal neutron flux of 4×10^{12} n cm^{-2} s^{-1} to two pneumatic-tube irradiation sites. In addition, a near-core irradiation facility delivers a thermal flux of 1×10^{13} n cm^{-2} s^{-1}.

Our group has its own computer-based gamma-counting system, purchased mostly from DOD/ONR funds. Its heart is a Nuclear Data 6700 multi-user, multi-task computer which can control up to 64 gamma-ray detectors and run up to 100 programs simultaneously. We currently have four large detectors (21-39% efficiency) hooked to it. The two smaller detectors (21-23%) are used for short irradiations; the two larger ones (34,39%) have sample changers and are used for long irradiations. Also attached to the ND 6700 are four control terminals, two hard disks (30 and 80 MB) for storing spectra temporarily, two magnetic tape drives for archiving spectra, and a printer. Altogether, the system is worth over $300,000, and is one of the most sophisticated in the Northeast.

After each spectrum is acquired, it is placed onto one of the disks. At the end of a series of counts, a program in the ND 7600 searches each spectrum for its peaks, determines the location, area, and uncertainty of each, and stores the results in a summary file on disk. An edited version of the summary file is transferred by wire to a PRIME 550 computer owned by the Center for Atmospheric Chemistry Studies, where another program calculates the elemental concentrations for each peak of interest.

Our group also has a sophisticated word/data-processing system from CPT which was purchased from the same ONR/DOD funds as the gamma-counting system was. The system consists of a central processor with dual high-density floppy disks, a 10-megabyte hard disk, three terminals, plus matrix and rotary printers. The central processor is connected to our PRIME 550 computer, from which it receives and prints large files of data in a form that is easy to read. Thus, we have a true fused word/data-processing system of high order.

Also in the RINSC are two chemical laboratories, a large Class 100 clean laboratory, three smaller clean benches, and a small machine shop. A larger machine shop is located on the Main Campus in Kingston. A new 550-ft^2 laboratory is presently being built for our group in the basement of the RINSC, and should be ready in fall 1986.

The RINSC also contains a complete atomic absorption laboratory, with three Perkin-Elmer instruments (Models 503, 603, and 5000), HGA-2000 a..d HGA-2100 heated graphite atomizer attachments, Models AS-1 and AS-40 sample changers, an HGA-500 programmer, two LFE model LTA-550 low-temperature ashers, and other accessories. For a standard user fee, this laboratory is available to all GSO

65

investigators. Another AA unit is available for a fee at the Marine Ecosystems Research Laboratory on campus.

For measuring sulfate, one of the chemistry laboratories has a Varian Series 634 UV-visible spectrophotometer with autosampler and DR37 digital printer. Other facilities available through the Center for Atmospheric Chemistry Studies and the Graduate School of Oceanography include an Alden facsimile machine for receiving meteorological maps and two electron microscopes, one with microprobe attachment.

D. CURRENT SUPPORT AND PENDING PROPOSALS

Dr. Kenneth A. Rahn - Research Professor, University of Rhode Island

Title	Agency	Duration	Amount	P.I.Time
		Current support		
Arctic Haze: Natural or Pollution?	ONR	1 Oct 1983-31 March 1987	$431,196 ($133,442 FY86)	4,3,3 mo.
Elemental tracers for local vs. distant source areas of pollution aerosol in the Northeast	OEUI (Ohio Electric Utility Institute)	1 May 1985-no ending date	$ 65,000	2 mo.
Elemental tracers of source regions of contaminants in precipitation	DOE	1 Nov 1984-31 May 1987	$107,900	3 mo.
Analyzing and interpreting PRECP and GALE filters	NOAA	15 Jan 1986-30 Sept 1986	$ 9,966	1 mo.
Local and distant sources of contaminants in rain and air of the Lower Hudson Valley	Hudson River Foundation	12 months	$52,624	2 mo.
Further development of regional elemental tracers for contaminants in precipitation	EPA	22 Sept 1986-21 Sept 1988	$209,385	3,3 mo.
Sources of suspended particulate in a coal mine	US Bureau of Mines	1 April 1986-30 Nov 1986	$ 4250	-

Pending applications

A study of equipment and personnel needed for Rhode Island to monitor ambient radioactivity rapidly in a nuclear emergency	RIAEC, RIDOH, RIEMA	6 months	$21,736	3 mo.
Arctic Haze: Natural or Pollution?	ONR (this proposal)	1 Oct 1986 - 30 Sept 1989	--	3,3,3 mo.

E. BUDGETS - FY87, 88, 89

Budget - FY1987 (January - September)

(1) <u>Salaries</u>

Principal Investigator Dr. Kenneth A. Rahn Research Professor - 3 months	$13,000	
Co-Principal Investigator Dr. Douglas H. Lowenthal Marine Scientist - 9 months	24,000	
Administrative Assistant Ms. Diane M. Tully 4 months	6,000	
Graduate student - Spring and summer Level I	8,200	
TOTAL SALARIES		$51,200

(2) <u>Staff Benefits</u>

22% of nonclassified ($37,000)	8,140	
32% of classified ($ 6,000)	1,920	
TOTAL STAFF BENEFITS		$10,060

(3) <u>Permanent equipment</u>

Freeze-drier (Fisher Scientific Co.)	9,000	
2 Rotron DR4R58 pumps for Barrow	2,400	
TOTAL PERMANENT EQUIPMENT		$11,400

(4) <u>Expendable equipment and supplies</u>

Laboratory chemicals, glassware, etc.	1,000	
Sampling supplies	500	
Computer supplies (tapes, paper, etc.)	1,000	
TOTAL EXPENDABLE EQUIPMENT AND SUPPLIES		$ 2,500

(5) Travel

Domestic:
Miscellaneous meetings   2,000
2 RT West Coast-Providence & 28 days perdiem   2,500
   (2-week visit of two Chinese scientists)

                              TOTAL DOMESTIC TRAVEL   4,500
Foreign:
1 RT Providence-Barrow & 5 days perdiem   2,500
1 RT Providence-Grenoble (arrange for transfer   1,500
   of ice-core samples)

                              TOTAL FOREIGN TRAVEL   4,000

                              TOTAL TRAVEL $ 8,500

(6) Publication Charges $ 1,500

(7) Other
Misc. sampling supplies for Barrow $ 500
Computer - Bay Campus   1,000
Telephone   500
Meteorological maps   500
Illustration services   500
Tuition for graduate student   1,900
Freight   500
AA charges ($4/hr x125 hr)   500

                              TOTAL OTHER $ 5,900

(8) Indirect charges

50% of MTDC ($ 77,760) $38,880

                              TOTAL COSTS $129,940

Budget - FY1988

(1) <u>Salaries</u>

Principal Investigator Dr. Kenneth A. Rahn $13,000
 Research Professor - 3 months

Co-Principal Investigator Dr. Douglas H. Lowenthal 33,000
 Marine Scientist - 12 months

Administrative Assistant Ms. Diane M. Tully   6,000
 4 months

Graduate student - 12 months   12,000
 Level I

                              TOTAL SALARIES $64,000

(2) <u>Staff Benefits</u>

22% of nonclassified ($46,000)   10,120
32% of classified   ($ 6,000)   1,920

                              TOTAL STAFF BENEFITS $12,040

(3) <u>Permanent equipment</u> - None

(4) <u>Expendable equipment and supplies</u>

Laboratory chemicals, glassware, etc.   2,000
Sampling supplies   1,000
Computer supplies (tapes, paper, etc.)   2,000

                              TOTAL EXPENDABLE $ 5,000
                              EQUIPMENT AND SUPPLIES

71

(5) <u>Travel</u>

<u>Domestic:</u>
Miscellaneous meetings   2,000

                              TOTAL DOMESTIC TRAVEL   2,000
<u>Foreign</u>:
1 RT Providence-Barrow & 5 days perdiem   2,500
2 RT Providence-Oslo (Fourth Arctic Air   4,000
        Chemistry Symposium)

                               TOTAL FOREIGN TRAVEL   6,500

                               TOTAL TRAVEL $ 8,500

(6) <u>Publication Charges</u> $ 1,500

(7) <u>Other</u>
Misc. sampling supplies for Barrow   500
Computer - Bay Campus   2,000
Telephone   500
Meteorological maps   500
Illustration services   500
Tuition for graduate student   3,800
Freight   500
AA charges ($4/hr x125 hr)   500

                               TOTAL OTHER $ 8,800

(8) <u>Indirect charges</u>

50% of MTDC ($ 96,040) $48,020

                               TOTAL COSTS $147,860

72

Budget - FY1989

(1) <u>Salaries</u>

    Principal Investigator Dr. Kenneth A. Rahn $14,000
     Research Professor - 3 months

    Co-Principal Investigator Dr. Douglas H. Lowenthal   35,000
     Marine Scientist - 12 months

    Administrative Assistant Ms. Diane M. Tully   7,000
     4 months

    Graduate student - 12 months   13,000
     Level I

                TOTAL SALARIES $69,000

(2) <u>Staff Benefits</u>

    22% of nonclassified ($49,000)   10,780
    32% of classified   ($ 7,000)   2,240

               TOTAL STAFF BENEFITS $13,020

(3) <u>Permanent equipment</u> - None

(4) <u>Expendable equipment and supplies</u>

    Laboratory chemicals, glassware, etc.   2,000
    Sampling supplies   1,000
    Computer supplies (tapes, paper, etc.)   2,000

               TOTAL EXPENDABLE $ 5,000
               EQUIPMENT AND SUPPLIES

(5) Travel

Domestic:
    Miscellaneous meetings   2,000

                      TOTAL DOMESTIC TRAVEL 2,000

Foreign:
    1 RT Providence-Barrow & 5 days perdiem   2,500
    1 European meeting   2,000

                      TOTAL FOREIGN TRAVEL 4,500

                      TOTAL TRAVEL $ 6,500

(6) Publication Charges $ 1,500

(7) Other
    Misc. sampling supplies for Barrow   500
    Computer - Bay Campus   2,000
    Telephone   500
    Meteorological maps   500
    Illustration services   500
    Tuition for graduate student   4,000
    Freight   500
    AA charges ($4/hr x125 hr)   500

                  TOTAL OTHER $ 9,000

(8) Indirect charges

    50% of MTDC ($100,020) $50,010

                  TOTAL COSTS $154,030

F. COMMENTS ON THE BUDGETS

FY1987

This budget is for nine months (January - September 1987), the first three months of the fiscal year having been funded from the FY1986 budget. As many charges as possible have been scaled downward accordingly. Salaries are higher than before, K. Rahn having been promoted and D. Lowenthal having received his Ph.D. Costs for graduate students have also risen.

Concerning equipment, we are requesting a freeze-drier ($8000) for processing the 100-200 ice-core samples as well as snow samples from Barrow. This item is truly needed - we have one freeze-drier already, but it is totally tied up with our acid-rain work. We are also requesting $2400 for two replacement pumps for air sampling at Barrow. Both current ones have broken down; one is replaced temporarily.

Concerning travel, we are requesting $2500 to support two Chinese scientists visiting us for two weeks. This visit is important, as it will ensure continued cooperation with Zhao Dianwu, and aerosol samples from north and south China, some of which can be used to further verify the all-important CUSSR signature. In return for this investment, Zhao Dianwu will pay for a return visit of K. Rahn and an associate. Under foreign travel, we are requesting one trip to Barrow for snow sampling, and a visit to Grenoble to arrange for the transfer of the ice-core samples from Nordauslandet.

FY1988

Salaries as before; no permanent equipment requested.

Under travel, one snow-sampling trip to Barrow requested, as well as funds for K. Rahn and D.H. Lowenthal to participate in the Fourth Arctic Air Chemistry Symposium in Oslo. All other costs are standard.

FY1989

Salaries as before; no permanent equipment requested.

Under travel, another snow-sampling trip to Barrow requested, as well as one European meeting for K. Rahn. All other costs are standard.

75

G. BIOGRAPHICAL INFORMATION

NAME: Kenneth A. Rahn

EDUCATION: Massachusetts Institute of Technology
               B.S. in Chemistry, 1962

               University of Michigan
               Ph.D. in Meteorology, 1971

PROFESSIONAL
EXPERIENCE:
1983-Present   Research Professor, Graduate School of Oceanography,
               University of Rhode Island

1980-1983   Associate Research Professor, Graduate School of
               Oceanography, University of Rhode Island

1979 (Summer) Visiting Scientist, Norwegian Institute for Air
               Research, Lillestrom, Norway

1976-1979   Research Associate, Graduate School of Oceanography,
               University of Rhode Island

1975-1976   Invited Visiting Scientist, Max-Planck-Institut fur
               Chemie, Mainz, W. Germany

1973-1975   Research Associate, Graduate School of Oceanography,
               University of Rhode Island

1971-1973   Research Associate, Institute for Nuclear Sciences,
               University of Ghent, Belgium

1968-1971   Graduate Assistant, University of Michigan, Ann
               Arbor, Michigan

1970 (Summer) Lawrence Radiation Laboratory, Livermore, California

1963-1968   Science and Mathematics teacher, Classical High School,
               Providence and Barrington College, Barrington, Rhode
               Island

PROFESSIONAL   American Chemical Society
SOCIETY   American Association for the Advancement of Science
MEMBERSHIPS: American Meteorological Society
               Gesellschaft fur Aerosolforschung

PUBLICATIONS:

             JR = Journal article, refereed
            JNR = Journal article, nonrefereed
             P = Popular article
            CH = Chapter of book
            CP = Conference proceedings
             R = Report

JR   Dams R., Robbins J.A., Rahn K.A. and Winchester J.W. (1970)
            Nondestructive neutron activation analysis of air pollution par-
            ticulates. Anal. Chem. 42, 861.

CP   Dams R., Rahn K.A., Robbins J.A., Nifong G.D. and Winchester J.W. (1971)
            Multi-element analysis of air pollution particulates by non-
            destructive neutron activation. Proceedings of the Second
            International Clean Air Congress, eds. H. M. Englund and W.T.
            Beery, pp. 509-516. Academic Press, New York.

JR   Harrison P.R., Rahn K.A., Dams R., Robbins J.A., Winchester J.W., Brar
            S.S. and Nelson D.M. (1971) Areawide trace metal con-
            centrations in Northwest Indiana as determined by multielement
            neutron activation analysis: a one-day study. J.Air Poll.
            Contr. Assoc. 21, 563.

JR   Rahn K.A., Dams R., Robbins J.A. and Winchester J.W. (1971) Diurnal
            variations of aerosol trace element concentrations as deter-
            mined by nondestructive neutron activation analysis. Atmos.
            Environ. 5, 413.

JR   Dams R., Rahn K.A., Nifong G.E., Robbins J.A. and Winchester J.W.
            (1971) Nondestructive multielement analysis of air pollution
            particulates. Isotopes and Radiation Technology 9, 54.

JR   Rahn K.A., Wesolowski J.J., John W. and Ralston H.R. (1971) Diurnal
            variations of aerosol and trace element concentrations in
            Livermore, California. J. Air Poll. Contr. Assoc. 21, 406.

CP   Dams R., Robbins J.A., Rahn K.A. and Winchester J.W. (1971)
            Quantitative relationships among trace elements over
            industrialized Northwest Indiana. In: Nuclear Techniques in
            Environmental Pollution, International Atomic Energy Agency,
            Vienna.

JR   Dams R., Rahn K.A. and Winchester J.W. (1972) Evaluation of filter
            materials and impaction surfaces for nondestructive neutron
            activation analysis of aerosols. Env. Sci. Technol. 6, 441.

JR   John W., Kaifer R., Rahn K. and Wesolowski J.J. (1973) Trace element
          concentrations in aerosols from the San Francisco Bay area.
          Atmos. Environ. 7, 107.

CP   Rahn K., Demuynck M., Dams R. and DeGraeve J. (1973) The chemical com-
          position of the aerosol over Belgium. In: Proceedings of the
          Third International Clean Air Congress, Dusseldorf, Germany, C81-C84,
          VDI-Verlag GmbH, Dusseldorf, West Germany.

CP   Heindryckx R., Demuynck M., Dams R., Janssens M. and Rahn K.A. (1973)
          Mercury and cadmium in Belgian aerosols. In: Colloquium on the
          Problems of the Contamination of Man and His Environment by Mercury
          and Cadmium, Luxembourg, July 1973, Sponsored by the Commission of
          the European Communities, Directorate Health Protection.

JR   Rahn K.A., Beke G. and Windels G. (1974) An automatic filter changer for
          collection of short-period high-volume aerosol samples. Atmos.
          Environ. 8, 635.

CP   Rahn K.A., Borys R.D. and Duce R.A. (1975) The University of Rhode
          Island's air sampling program in the Northwest Territories. In:
          Report of Polar Meteorology Workshop, Reno, Nevada, 1975. Desert
          Research Institute Laboratory of Atmospheric Physics, Technical
          Report, Series P (Physical Sciences) No. 18, pp 85-87.

CP   Harrison P.R., Rahn K.A., Dams R., Robbins J.A. and Winchester J.W. (1975)
          Areawide trace metal distributions in northwest Indiana aerosols.
          In: Trace Contaminants in the Environment, American Institute of
          Chemical Engineers Symposium Series, No. 149, pp. 19-25, Andre F.
          LeRoy, Ed.

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84

[PII Redacted]

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B.A. Tufts University, 1970 (Philosophy-Biology)
M.S. Graduate School of Oceanography,
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     University of Rhode Island, 1986 (Atmospheric Chemistry)

PROFESSIONAL
EXPERIENCE:

Oct. 1981-   Marine Research Specialist V, Graduate School
                 of Oceanography, University of Rhode Island.
                 - Chemical analysis of atmospheric aerosol
                   samples, computer analysis and statistical
                   interpretation leading to publications on
                   sources of aerosol pollution.

June 1978-   Research Assistant, Graduate School of Oceanography,
Aug. 1980   University of Rhode Island.
                 - Investigation of the ecological state of local
                   plankton communities; development of an approach
                   to evaluate pollution effects.

Sept. 1976-   Research Assistant, Marine Ecosystems Research Laboratory,
June 1978   University of Rhode Island
                 - Conducted experiments in artificial microcosms to
                   evaluate the effects of oil pollution on bacterial
                   and plankton populations under controlled conditions.

Jan. 1974-   Research Assistant, Graduate School of Oceanography,
Aug. 1976   University of Rhode Island
                 - Analytical and physical-chemical studies on phosphorus
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Sept. 1973-   Instructor, University of Rhode Island
Dec. 1973   - Organic Chemistry

PUBLICATIONS:

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APPENDIX

Reprints of selected publications

PARTICLE-SIZE DISTRIBUTIONS

OF THE

ARCTIC AEROSOL

BY

NOELLE F. LEWIS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

OCEANOGRAPHY

UNIVERSITY OF RHODE ISLAND

1985

90

ABSTRACT

Arctic haze has existed in the Arctic for many years. It occurs during the winter months and is caused by meteorological conditions that transport anthropogenic aerosols with unusual efficiency. The composition and origin of Arctic haze have been determined, and its chemical, physical and biological effects are beginning to be understood. This study describes the particle-size distribution of Arctic haze, the particle-size distribution of its source aerosol, and the changes in particle-size distributions during long-range transport from the source.

Aerosols were sampled with replicates of Sierra Cascade Impactor Model 235. Impaction-surface coatings were evaluated and a new coating was developed. Whatman No. 41 impaction surfaces immersed in an equal mixture of glycerol and de-ionized water were found to be superior to previous systems and were used for this study. The size distributions for 37 elements (determined by neutron activation) of the Arctic haze in Barrow, Alaska, and for mid-latitude aerosols, in Berlin and Mainz, West Germany, and Rorvik, Sweden, representing source-type aerosols, were measured.

This study agreed with previous studies in indicating that Arctic haze is a seasonal phenomenom. It showed that the Arctic aerosol, although primarily submicron, does contain supermicron particles. Using selected elements, the Arctic aerosol was partitioned into four inorganic components: marine, crustal, primary-pollution and sulfate. The primary pollutants were the only component showing an increase in the fine-particle fraction from winter to early spring (December to March).

The effect of long-range transport and aging on size distributions of the crustal, primary-pollution and sulfate components indicated that the particle-size distribution changed more during transport from Central Europe to Sweden than during transport from Sweden to Barrow. Overall, approximately 74% of the material greater than 2.0 µm in diameter was lost during transport from Central Europe to Barrow.

It was estimated that elemental ratios used as regional atmospheric tracers in the Arctic changed by 10% to 40% in the most extreme case, relative to an urban aerosol such as Berlin, but by only 0% to 13% relative to regional aerosol of southern Sweden.

REGIONAL SOURCE APPORTIONMENT AND RELATED

STATISTICAL TOPICS

BY DOUGLAS H. LOWENTHAL

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

OCEANOGRAPHY

UNIVERSITY OF RHODE ISLAND

1986

93

ABSTRACT.

This dissertation evaluates the feasibility of receptor modeling for apportioning regional sources of pollution aerosol. Receptor modeling is used to determine origins of atmospheric aerosol from measured or inferred source characteristics and was first applied in urban areas to resolve the contributions from similar types of sources. The increasingly recognized role of long-range transport of atmospheric pollutants calls for new developments in this field. Regional receptor modeling is needed to determine origins of phenomena such as "Arctic Haze" and "Acid Rain" which result from long-range transport of pollution aerosols and their precursors.

The regional problem is fundamentally different from the urban case. Because most regions of North America and Eurasia have roughly similar individual sources, such as autos, incinerators or power plants, regional origins of pollution aerosol cannot be determined by discriminating individual source types. It is therefore necessary that true regional elemental signatures be determined. Part of the solution to regional pollution problems lies in developing receptor models which will distinguish regions rather than specific source types.

Statistical aspects of regional receptor modeling are examined to validate regional apportionments and refine the techniques needed to produce them. Various methods are used to apportion the regional sources of aerosol in the North American Arctic. Techniques are developed to account for systematic error in receptor models. The

94

suitability of the factor analysis model for urban and regional problems is evaluated.

A combination of statistical and empirical tests demonstrates that: 1) valid signatures can be derived from fewer than 10 carefully chosen samples, 2) the scale of signatures does not affect elemental apportionments significantly, 3) signatures derived for eastern North America are not significantly collinear, are distinct in practice and cannot be interchanged without degrading apportionments, 4) regional apportionments are stable with respect to random perturbations in sample and signatures, and 5) strong local sources of a single element neither mask the character of the aerosol nor affect regional apportionments significantly. The regional apportionment system is stable, self-consistent, and reasonable.

Regional signatures determined from samples taken in Europe, North America and the European Arctic were used to apportion regional contributions to pollution aerosol at Barrow, Alaska during the winter of 1979-80. Factor analysis, discriminant analysis and Chemical Element Balance (CEB) apportionment suggested that Europe and the Soviet Union were the major sources of pollution aerosol during this period.

A critical evaluation of the CEB model showed that collinearity significantly increases uncertainties of estimated source contributions of sources with similar signatures. Collinearity and systematic errors in source profiles increase propagated uncertainties in source-strength estimates. A procedure was developed to account for systematic errors and calculate realistic uncertainties of estimated source contributions.

95

The utility of factor analysis in urban and regional receptor modeling was evaluated using simulated data. Source contributions were estimated to no better than a factor of two depending on the degree of collinearity, serial correlation of source strengths, measurement error and random variation in the source compositions. Previously measured regional profiles were confirmed by comparing them to the principal components of elemental data from regionally representative samples at a number of sites.

SCIENCE

Elemental Tracers of Distant
Regional Pollution Aerosols

Kenneth A. Rahn and Douglas H. Lowenthal

Elemental Tracers of Distant Regional Pollution Aerosols

Kenneth A. Rahn and Douglas H. Lowenthal

The routine transport of pollution aerosol through long distances is increasingly recognized as an important aspect of atmospheric science. Atmospheric transport on the scale of 1000 to 10,000 km is now invoked regularly to explain the results of aerosol studies in rural and remote areas (*1*).

often pass over several strong source areas in their last few hundred kilometers. No available transport model can reliably apportion the contributions of these sources to the final sulfate, acid, or other ubiquitous constituents of the pollution aerosol.

There is thus a need for a more direct

Summary. A seven-element tracer system shows that regional pollution aerosols of both North America and Europe have characteristic signatures that can be followed into remote areas up to several thousand kilometers downwind. In aerosols of mixed origin, regional contributions to the tracer elements can be resolved by least-squares procedures. After transport of several hundred kilometers, secondary sulfate can also be apportioned satisfactorily. Regional elemental tracers thus offer a way to determine the sources of pollution aerosol in important areas such as the northeastern United States, Scandinavia, and the Arctic.

But long-range transport has created a new set of interpretive problems. While it is relatively easy to identify pulses of transported pollution aerosols in remote areas which are otherwise clean, it is often d... ult or impossible to pinpoint the sou . areas of these aerosols. (At distances of a few hundred kilometers or more, source areas are normally much more important than point sources.)

Sheer distance can cause problems. For example, it has been extremely difficult to decide whether the important sources of pollution aerosol observed at Barrow, Alaska, are located in North America, Europe, or Asia. With air-mass trajectories from these sources being 5000 to 10,000 km or more in length and representing travel times of 5 to 10 days or more, pure meteorological techniques have not led to a consensus about even the continents of origin, much less particular regions within the continents (*2*).

The configuration of sources can also make identification difficult. In the northeastern United States, for example, where the source areas of acid aerosol and precipitation are currently in dispute, distances of transport are much shorter (1000 km or less) but the spatial pattern of sources is complex. As a result, trajectories to areas of concern such as the Adirondacks or New England

way to identify distant sources of pollution aerosol. Such a capability would be of practical as well as scientific importance, because it could be extended ultimately to determining source areas of acid precipitation. It may cost as much as $20 billion to $100 billion to reduce emissions of sulfur dioxide in the eastern United States over the next decade; controlling the wrong sources would be a very costly error.

We feel that the use of chemical tracers in the aerosol itself holds considerable promise. This article deals with our efforts to develop regional elemental tracers of pollution aerosol; eventually, organic and stable isotopic tracers can probably be developed and used analogously.

Prospects for Regional Elemental Tracers of Pollution Aerosol

Pollution aerosol contains all elements; no true tracers, or elements unique to specific source areas, exist. But it is reasonable to expect the proportions of at least some elements to vary with source area because different areas have different mixes of the major aerosol sources (combustion, industry, transportation, and so on), different mixes of

fuels, fuels from different origins, different industrial bases, and different degrees of pollution control. However, the number of regional elemental signatures, the magnitude of their differences, and the elements involved cannot be predicted; they must be determined empirically.

In general, regional tracers are constructed and used quite differently from urban tracers. Elemental signatures used to deduce sources of urban aerosol by receptor-oriented techniques (*3*) are usually derived for either point sources or specific types of sources (automotive exhaust, for example). Regional aerosols, by contrast, are mixes of many sources and should thus resemble one another much more than signatures within an urban region should. Similarities among pollution aerosols have been recognized for years (*4*), and many have doubted whether useful regional differences could be found. We have determined that characteristic regional signatures do exist, many of which are very different from one another.

The two keys to deriving regional signatures are finding the right elements and handling the data with the appropriate statistical techniques. The "marker-element" approach sometimes used in urban studies (where the contribution of a source is evaluated by a single element) cannot be used with regional signatures because of their great similarities. The opposite approach, constructing signatures from all available elements, is practiced in some urban studies but adds too much noise to regional pollution signatures The best approach seems to be a compromise—limit regional signatures to those few elements with the greatest tracer power.

Several requirements should be met by elements and signatures before they can be used in a regional tracer system: the elements should be pollution-derived, sampled and measured accurately, emitted stably and homogeneously in each region, and present on particles small enough to be transported long distances; each signature should remain recognizable during transport. Our preliminary assessment indicates that all these requirements are met adequately; we illustrate several of them in the discussion that follows. Nevertheless, some of these requirements, such as conservation of proportions during transport, are sufficiently critical that we have built routine checks into our operating system.

A Seven-Element Tracer System for Pollution Aerosol

The first regional tracer was the noncrustal Mn/V ratio (5), which was designed to determine whether Arctic aerosol originated mainly from Europe or eastern North America. The noncrustal Mn/V ratio demonstrated the general feasibility of regional elemental tracers and stimulated the development of more sophisticated tracing systems. At present, we are using a seven-element tracer system involving As, Sb, Se, Zn, In, noncrustal Mn, and noncrustal V. The design of this system and several of its applications are discussed below.

These seven elements were chosen from the 40 to 45 that we have measured by neutron activation as best meeting the criteria of being pollution-derived, fine-particle (6), and accurately analyzable (7). Potential tracers rejected because of larger analytical uncertainties included Cu, Ni, Ga, Mo, Ag, Cd, Sn, W, Au, and Hg. With better analysis, any or all of these might be included in the system. Lead and elemental carbon are strong candidates which should also be investigated. Indium, whose analysis is poorer than those of the other six elements, was retained because of its great utility in tracing nonferrous smelters (8).

Our regional signatures consist of six elemental ratios to Se. Ratios are used to normalize for variable meteorological effects such as dispersion and removal. Se is used in the denominator because it is a general pollutant found at similar concentrations in diverse source areas and hence will not bias the ratios toward any particular region. In spite of Se's ubiquitous but modest vapor phase of 15 to 30 percent near the surface (9) and its natural sources such as volcanoes, it works well as a normalizing element in regions as remote as the Arctic in winter. We tested Zn as an alternative denominator (because of its similarly low coefficient of variation) and obtained the same results as with Se. Other general pollution
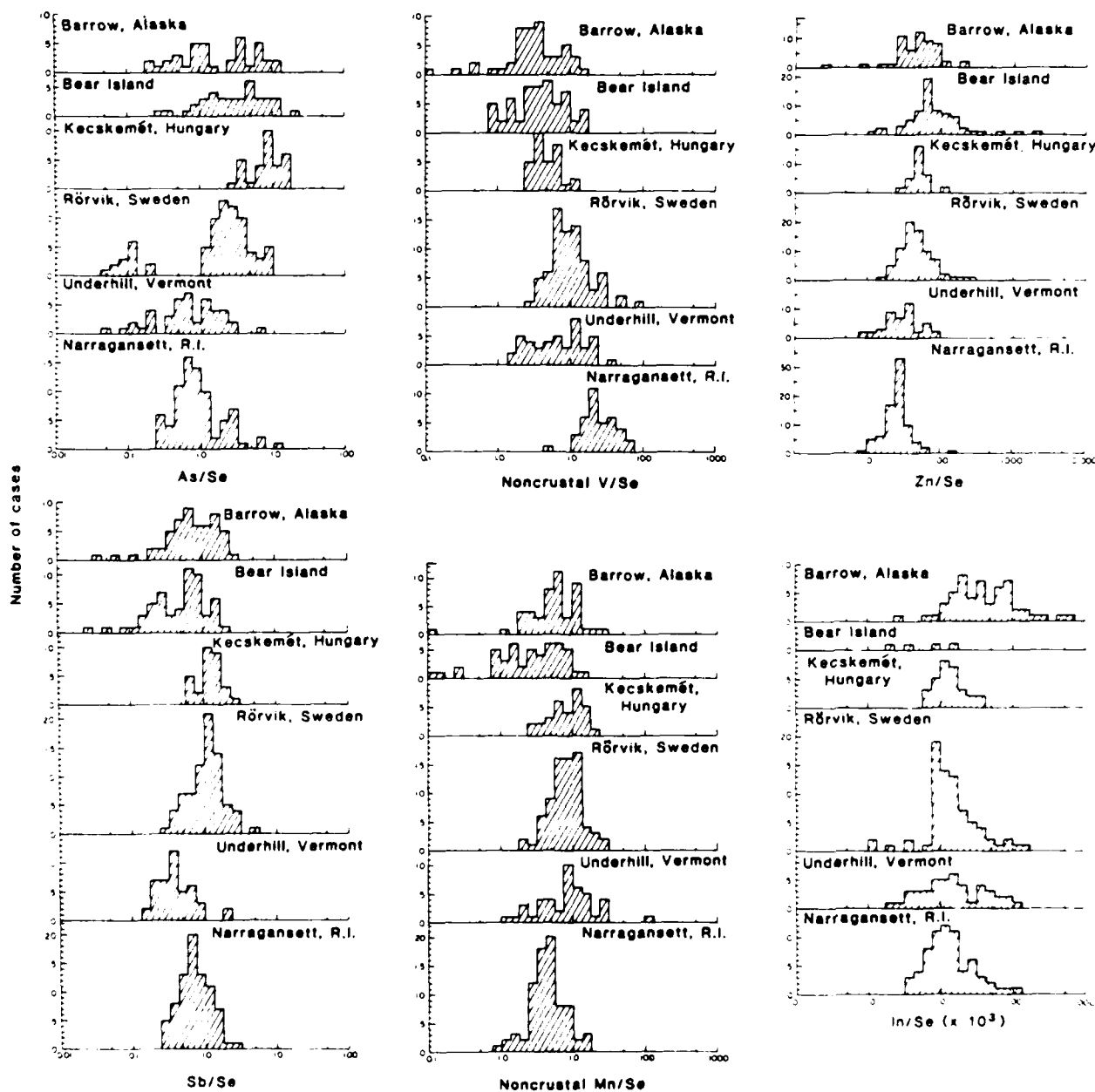

Fig. 1. Frequency distributions of six elemental ratios at six sites in eastern North America, Europe, and the Arctic

elements such as Pb or C might also be considered for the denominator.

The signature of a source region cannot be derived in a completely straightforward fashion because most regions can be affected by pollution aerosols transported from other regions. To eliminate such interference, we are developing a protocol which involves multiple samples at multiple sites inside and outside the region. At each site, at least 100 (ideally) daily samples are taken and analyzed for the tracer elements. Logarithmic frequency distributions of the various X/Se ratios are then constructed and examined for the presence of modes, or maxima, which represent characteristic aerosols for the sites. The meteorological and chemical characteristics of the samples in a mode usually give a good idea of its source. By combining the modal information from several sites in a region, its aerosol may usually be distinguished from those transported from neighboring regions. As a final check, regional signatures are verified by sampling downwind of the region. This also shows whether any elemental ratios change significantly during transport.

To date, we have used filter samples of total aerosol for our tracer system. In effect, this provides size-segregated data because the tracer elements chosen are mostly submicrometer. True fine-particle samples would probably improve the tracer system by reducing the variability of elemental ratios and allowing mixed-mode elements such as Fe, Co, and Cr to be considered. But how much the improvement would be is not yet known, and size-segregated samples are much smaller and not readily available from many regions of interest. When elemental tracer techniques are eventually applied to precipitation, total aerosol will be a more appropriate reference than fine-particle aerosol, for coarse particles are scavenged more efficiently by precipitation than are fine particles.

Factor analysis, while useful for understanding broad elemental relations and the general sources of pollution aerosol of a site, has not been particularly successful in selecting elements as tracers or defining regional signatures. The reason for this seems to be that any technique which is based solely on single measures of similarity between elements (such as correlations) in a collection of samples does not adequately reveal the complex relations implicit in mixed frequency distributions.

Modes in Pollution Aerosols from North America, Europe, and the Arctic

Figure 1 shows the six X/Se distributions for six sites at which we have reasonable amounts of data: Narragansett, Rhode Island, and Underhill, Vermont, in eastern North America; Kecskemét, Hungary, and Rörvik, Sweden, in Europe; and Barrow, Alaska, and Bear Island, Norway, in the Arctic (10). Depending on element and location, one or more modes are seen in each distribution. The modes are reasonably symmetric (that is, log-normal), with geometric standard deviations of 1.4 to 1.6 (68 percent of the points found within a total factor of 2 to 3). Some modes have geometric standard deviations as low as 1.2. The presence of these modes shows that a few major types of pollution aerosol are found at each site.

More types of pollution aerosol may be present at a site than are revealed directly by the major modes, however. Broader-than-normal modes may be composed of two or more unresolved modes, as seems often to be the case for Zn/Se and Sb/Se, for example. Small features may represent infrequent appearances of aerosols which are more important elsewhere. An example of this is the small upper mode of As/Se at Rorvik (ratios of 8 to 10), which coincides with the principal mode (6 to 12) at Kecskemét (we show below that the upper mode at Rörvik was created by a pulse of aerosol from eastern Europe). Another example is the low shoulder of Zn/Se at Narragansett (ratios of 10 to 20), which has been resolved into a discrete mode by subsequent shorter period samples. The real number of modes in most distributions is not known and may be considerably larger than the number apparent from Fig. 1.

Membership in most modes is organized; that is, samples in a certain mode of one distribution are usually found together in other distributions. For example, the samples from eastern Europe which comprise the upper As/Se mode of Rörvik also comprise the low shoulder of noncrustal V/Se there (ratios of 3 to 6). This illustrates that well-defined pol-

Table 1. Geometric mean elemental signatures for source aerosols in North America and Europe (geometric standard deviations in parentheses).

Source	N	As/Se	Sb/Se	Noncrustal V/Se	Zn/Se	Noncrustal Mn/Se	In/Se (×1000)
				Individual sources			
SCANS	5	2.8 (1.3)	0.94 (2.0)	24 (1.3)	43 (1.5)	5.2 (1.8)	9.5 (1.7)
WEURS	5	1.88 (1.2)	1.01 (1.4)	5.8 (1.3)	37 (1.1)	6.5 (1.2)	13.1 (1.6)
WEURH	5	3.5 (1.1)	0.75 (1.3)	7.2 (1.8)	56 (1.4)	6.8 (1.7)	11.1 (2.2)
EEURF	5	7.2 (1.2)	1.33 (1.3)	7.8 (1.2)	54 (1.1)	10.0 (1.2)	13.1 (1.3)
EEURS	3	7.3 (1.1)	1.73 (1.1)	4.8 (1.2)	66 (1.1)	13.7 (1.2)	15.1 (1.2)
EEURH	4	8.9 (1.0)	1.18 (1.1)	5.2 (1.3)	48 (1.1)	8.9 (1.8)	9.8 (1.4)
NE	4	0.130 (1.4)	0.45 (1.3)	11.3 (1.2)	32 (1.2)	9.2 (1.3)	9.8 (1.9)
BOS	3	0.68 (1.5)	0.82 (1.8)	35 (1.2)	37 (1.1)	4.1 (1.2)	5.3 (1.1)
NYC	3	1.10 (1.1)	1.63 (1.7)	11.1 (1.3)	40 (1.1)	6.5 (1.3)	9.6 (1.6)
WASH	4	1.46 (1.2)	0.82 (1.2)	9.9 (1.2)	22 (1.2)	4.0 (1.8)	7.1 (1.2)
INT	4	0.92 (1.2)	0.28 (1.4)	1.96 (1.4)	10.8 (1.3)	2.6 (1.5)	3.9 (1.7)
SONT	3	8.0 (1.2)	0.75 (1.2)	1.77 (1.9)	57 (1.1)	13.9 (1.1)	46 (1.7)
				Regional means			
SCANS	5	2.8 (1.3)	0.94 (2.0)	24 (1.3)	43 (1.5)	5.2 (1.8)	9.5 (1.7)
WEUR	10	2.6 (1.4)	0.87 (1.4)	6.4 (1.6)	45 (1.4)	6.6 (1.5)	12.1 (1.9)
EEUR	12	7.8 (1.2)	1.37 (1.2)	6.0 (1.4)	54 (1.1)	10.4 (1.5)	12.3 (1.3)
ECOAST	14	0.58 (2.9)	0.80 (1.8)	13.8 (1.7)	31 (1.3)	5.7 (1.6)	7.8 (1.6)
INT	4	0.92 (1.2)	0.28 (1.4)	1.96 (1.4)	10.8 (1.3)	2.6 (1.5)	3.9 (1.7)
SONT	3	8.0 (1.2)	0.75 (1.2)	1.77 (1.9)	57 (1.1)	13.9 (1.1)	46 (1.7)
				Continental means			
EUR	27	4.2 (1.8)	1.08 (1.5)	8.0 (1.9)	49 (1.3)	7.6 (1.6)	11.6 (1.6)
NAMER	21	0.93 (3.5)	0.65 (1.9)	7.1 (3.0)	28 (1.8)	5.6 (1.9)	8.8 (2.4)

lution aerosols with recognizable signatures do exist. As shown below, they can usually be identified with specific geographic source areas.

Regional Signatures of Pollution

Aerosols in North America and Europe

At present, we use the modes of Fig. 1 only qualitatively. To derive signatures of pollution aerosol for specific regions, we use subsets of the modes composed of samples deemed most representative. With experience, it should be possible to increase the numbers of samples used to define signatures.

We are currently working with 12 regional signatures, six from North America and six from Europe, as shown in Table 1. The signature of regional New England (NE) was derived from four daily samples at Underhill (4 to 7 August 1982), in aged Canadian air masses which had not been affected by the large nonferrous smelters of the Sudbury Basin. The outstanding feature of this signature is its low As/Se ratio, which we interpret as indicating minimal coal influence. We have also detected this signature in Narragansett and South Portland, Maine (the small low-As mode at Narragansett in Fig. 1 is associated with this kind of aerosol). The "Boston" (BOS) aerosol was derived from three daily samples at Narragansett when the winds came from the direction of Boston and Providence and SO$_2$ concentrations were high (20 July and 3 and 6 August 1982). The New York City (NYC) signature came from six semiweekly samples taken in midtown Manhattan during the 1977–1978 winter. In order to better apply this signature to summer samples elsewhere, we reduced its noncrustal V by 50 percent (11). To better simulate the regional signature near New York, we reduced the Zn, which is abnormally enriched in urban aerosol, by 30 percent (because roughly 30 percent of the Zn is from coarse particles and presumably local, not regional, there). The Washington, D.C. (WASH), signature came from grand averages of individual average concentrations from ten sites in the Washington area during August and September 1976 (12). As in New York, Zn was reduced by 30 percent in an attempt to represent aerosol from the central mid-Atlantic states. The interior (INT) signature was derived from four daily samples in Underhill, Vermont, in July 1982, when an unusually strong signal of coal was present and associated with winds from the south-southwest. This signature does not represent pure coal

emissions but rather an area where coal emissions are unusually strong. The Canadian smelter (SONT) signal was derived from three samples in southern Ontario roughly 300 km east-southeast of Sudbury (13). It is enriched in As and In. (The small groups of samples defining the signatures were representative distillations of larger sets of data; numbers of samples in each group were kept comparable for statistical purposes.)

The samples from Kecskemét and Rörvik allowed us to construct six regional signatures for Europe, three from the East and three from the West. Signature EEURH came from four samples associated with the most prominent mode of As/Se in Kecskemét. Signature EEURS came from three samples at Rörvik during the most intense "black episode" (14) of the past decade. As shown in Table 2, this aerosol was very different from that before and after the episode and had eastern European rather than western European characteristics.

These samples made up most of the small upper mode of As/Se at Rörvik shown in Fig. 1. Signature EEURF came from four samples at Ahtari, southern Finland, during the same black episode. Table 2 also shows these samples and how they closely resembled aerosol at Rörvik during the same period. The two signatures of western Europe, WEURS and WEURH, were derived from five samples at Rörvik when the winds were from the southwest and five samples at Kecskemét when the winds were from the west, respectively. For at least As/Se and noncrustal V/Se, these samples appeared in well-defined modes at the two sites. The last European signature is for Scandinavia (SCANS), as determined from periods of unusually high noncrustal V/Se at Rörvik, which usually coincided with weak circulation or winds from the north.

The western and eastern European signatures confirm the existence of general regional aerosols which appear at

Table 2. Episode of east European aerosol at Sweden and Finland.

Dates of sample (1982)	Sulfate (μg m^{-3})	As/Se	Sb/Se	Non-crustal V/Se	Zn/Se	Non-crustal Mn/Se	In Se ($\times 10^3$)
			Rörvik, Sweden				
11–13 January	2.4	3.0	0.67	15.4	69	13.1	17.4
13–15 January	5.4	9.6	2.4	50	52	26.5	31
15–18 January	12.9	4.0	0.8	5.2	49	6.0	< 3
18–20 January*	11.1	7.4	1.85	6.0	70	13.0	16.1
20–21 January*	19.5	8.2	1.68	3.8	65	11.7	12.8
21–22 January*	35.5	6.3	1.68	4.8	63	16.8	16.7
22–25 January	8.3	3.3	1.83	4.2	33	4.5	7.6
25–27 January	3.6	1.8	0.98	14.6	31	3.5	13.1
			Ähtäri, Finland				
17–18 January	6.5	3.4	0.60	9.4	54	3.8	7.2
18–19 January	5.3	2.6	0.64	8.0	66	5.7	11
19–20 January*	3.7	5.5	1.3	8.9	58	9.5	15
20–21 January*	19.4	6.6	1.6	5.7	52	13	13
21–22 January*	9.0	6.8	1.5	7.0	56	11	11
22–23 January*	17.8	5.9	1.6	8.3	52	10	10
23–24 January	0.95	4.6	0.86	10	52	7.6	18

*East European aerosol present.

Table 3. Two estimates of the relative discriminatory power of various elemental ratios on the 48 signature samples of Table 1.

| Elemental ratio omitted | Number of samples misclassified (out of 48) | | |
	With 12 individual signatures	With 6 regional signatures	With 2 continental signatures
	1	2	7
As/Se	6	13	13
Sb/Se	1	2	6
Noncrustal V/Se	3	6	7
Zn/Se	2	3	9
Noncrustal Mn/Se	1	4	7
In/Se	2	2	7
As/Se, noncrustal V/Se	13	19	10
Noncrustal Mn/Se. In Se*	2		
Sb/Se, Zn/Se*		5	
Sb/Se, Zn/Se, noncrustal Mn/Se. In Se*			8

*Ratios indicated by stepwise discriminant analysis to be lacking in discriminatory power

101

Table 4. Classification of nonsignature aerosol samples in North America and Europe.

Site	With 12 individual signatures		With 6 regional signatures		With 2 continental signatures	
	North America	Europe	North America	Europe	North America	Europe
Narragansett, R.I.	98	3	92	9	94	7
Underhill, Vermont	25	10	22	13	29	6
Rörvik, Sweden	21	45	19	47	28	38
Kecskemét, Hungary	0	22	0	22	0	22
With five regional signatures						
Bear Island, Norway (without In/Se)				1		31
Barrow, Alaska (without In/Se)				5		28
	SONT	NE	BOS	NYC	WASH	INT
Narragansett, R.I.	0	17	17	8	37	22
Underhill, Vermont	1	14	1	7	3	9

various sites in and around large source regions. Because the three eastern signatures are so similar, they can be combined into a general eastern European signature (EEUR), as shown in Table 1. Similarly, the two western European signatures can be combined into the general WEUR. As more data become available from eastern North America, it should be possible to construct general signatures there as well. For illustrative purposes, we have combined the four coastal signatures NE, BOS, NYC, and WASH into ECOAST, which is also shown in Table 1. (All samples from North America and Europe were combined to form the continental signatures NAMER and EUR.) Note that the principal modes of As/Se, noncrustal V/Se, and Zn/Se at Barrow and Bear Island agree quite well with the WEUR and EEUR modes at Rörvik and Kecskemét.

Some of the most significant features emerging for elemental tracers are that the tracing power varies widely from element to element, that most of the tracing power is vested in a very few elements, and that the discriminatory power of an element, as measured by the range of its X/Se ratio and its degree of modality, is similar at widely diverse sites. For example, As/Se and Zn/Se have, respectively, large ranges with

well-defined multiple modes and small ranges with single modes at most sites. Thus some elements are inherently much better tracers than others. The reasons for this are probably geochemical. They may be related to large-scale elemental variations in the earth's crust.

Table 3 illustrates two ways to measure the relative discriminatory power of tracer elements. In the first, linear discriminant analysis (15) on log-transformed data was used to classify the 48 signature samples of Table 1 into the 12, 6, and 2 groups shown in Table 3. Initially, all six of our X/Se ratios were used. Then the samples were reclassified with each of the ratios removed in turn. The greater the discriminatory power of a ratio, the more samples will be misclassified when it is removed. The results showed that As/Se and noncrustal V/Se had the greatest discriminatory power, Zn/Se had somewhat less power, and the other three ratios contributed little or nothing on the average. When both As/Se and noncrustal V/Se were removed, the extent of misclassification became greater than their summed individual effects. As a more sophisticated test of discriminatory power, stepwise discriminant analysis (16) was applied to the six ratios (log-transformed) as they were used to segregate the 48 samples

into groups of 12, 6, and 2 signatures. The results are shown at the bottom of Table 3. The only two ratios having good tracer power in all three cases were As/Se and noncrustal V/Se.

It may be possible to improve the discriminatory power of our ratios by using discriminant analysis in which elemental ratios are replaced by higher order terms as generated and selected by the group method of data handling (17). The discriminatory power of optimized functions of ratios seems to be at least 20 to 40 percent greater than that of linear functions. Products involving As/Se and noncrustal V/Se are the most useful.

Empirical confirmation that certain elements are crucial to a successful regional tracer system was obtained by comparing our experience in southern Sweden with results of Lannefors et al. (18), who took daily aerosol samples for 1 year at Sjöängen, 200 km northeast of Rörvik. Their data, which included S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb but lacked As, Se, Sb, and In, were unable to differentiate between aerosols from eastern and western Europe.

To test whether the criteria on which our seven-element tracer system was based—that the components be pollution-derived, fine-particle, and determined well by neutron activation—are unduly restrictive, we investigated the tracer power of nine other elements (Al, Sc, Cr, Co, Fe, La, Ce, Sm, Th) by means of stepwise discriminant analysis on the same 48 signature samples. These elements are as well determined as the seven basic tracers but are mostly coarse-particle in the aerosol (Cr, Co, and Fe usually have a fine-particle component and La and Ce occasionally do). In general, the tracer power of La, Ce, and Sc was comparable to or better than that of Sb, In, and noncrustal Mn but less than that of As, noncrustal V, and Zn. The Al, Sm, and Th appeared to have little promise as tracers, and Fe, Co, and Cr behaved in an intermediate fashion. We do not know how the apparent tracer power of La, Ce, and Sc is partitioned between their coarse- and

Table 5. Elemental concentrations in five source-area aerosols.

Element	Concentration (ng m⁻³)				
	NE	BOS	NYC	WASH	INT
As	0.060 ± 0.033	0.49 ± 0.15	2.0 ± 0.2	3.2 ± 0.9	1.54 ± 0.40
Sb	0.143 ± 0.048	0.83 ± 0.41	3.1 ± 0.6	2.1 ± 0.7	0.55 ± 0.20
Se	0.37 ± 0.20	1.00 ± 0.60	1.88 ± 0.42	2.4 ± 0.7	1.78 ± 0.79
Noncrustal V	4.0 ± 1.7	35 ± 6	20 ± 4	23 ± 8	3.4 ± 1.0
Zn	11.1 ± 4.3	37 ± 3	70 ± 17	60 ± 12	18.2 ± 8.0
Noncrustal Mn	2.2 ± 0.3	4.2 ± 0.8	13.0 ± 1.1	9.2 ± 3.4	4.3 ± 2.4
In	0.0028 ± 0.0001	0.0050 ± 0.0040	0.0160 ± 0.0032	0.020 ± 0.006	0.0064 ± 0.0006

102

fine-particle components. The fraction associated with coarse aerosol may be less useful than suggested by these signature samples, because coarse aerosol is not transported as efficiently as fine aerosol. Overall, it is probably prudent to measure as many elements as possible (both natural and pollution-derived) in the aerosol, with an eye toward occasions when they could be useful as tracers. Dust storms, volcanic eruptions, or bursts of aerosol from unexpected point sources of pollution may all provide transient aerosols with unusual signatures which could be understood by use of additional tracer elements.

Use of Regional Pollution Signatures to Classify Unknown Aerosol Samples

Once discriminant analysis has been used to determine classification criteria from samples with distinctive signatures, one may classify nonsignature samples into those groups. In principle, the origin of an aerosol sample could be determined from its chemical composition alone.

Table 4 shows the present status of geographic classification of unknown samples by our seven-element tracer system. In the upper part of the table, nonsignature samples from Narragansett, Underhill, Rörvik, and Kecskemét have been classifed as North American or European based first on 12 individual signatures, then on six regional signatures, and finally on the two continental signatures of Table 1. In general, the posterior probability for membership in one of the source groups was greater than 90 percent. All samples from Kecskemét were classified correctly (as European). At Narragansett, 90 to 95 percent were classified correctly (as North American). At Underhill and Rörvik, however, only 60 to 80 percent were classifed correctly. Similar results were obtained when the noncrustal Mn/Se and In/Se ratios were eliminated. Classifying samples by continent is a severe test, however, because it is much more difficult for entire continents than for regions to have distinct signatures.

The center of Table 4 shows how samples at Bear Island and Barrow were classified relative to the five most appropriate regional signatures (SCANS, WEUR, EEUR, ECOAST, INT). Only 1 of 32 (3 percent) and 5 of 33 (15 percent), respectively, were called North American. This confirms our earlier conclusions, reached independer 'ly, that Arctic pollution aerosol is stron ly Eurasian in origin (19).

The bottom of Table 4 illustrates how the nonsignature samples at Narragansett and Underhill were classified relative to the six North American signatures. At Narragansett, the four coastal signatures accounted for three-quarters of the cases, with the other quarter coming from the interior signature. This result confirms with multielemental data the conclusions about dominance of coastal aerosol reached earlier from noncrustal Mn and V alone (11). At Underhill, on the other hand, the most common signature is New England (40 percent), followed by other East Coast (30 percent) and the interior (25 percent). Considering Underhill's location in northern New England, this distribution of sources is reasonable.

Apportionment of Tracer Elements Among Regional Pollution Sources

Discriminant analysis is used to determine which of several signatures is most likely to account for an aerosol sample. In actuality, however, most aerosol samples come from more than one source, either because of the history of the air mass or because of changes in it during sampling. By using least-squares techniques similar to those employed in previous chemical element balance analyses (3), a sample can be apportioned among the various regional aerosols which may have contributed to it (20). For the elemental concentrations of five regional aerosols listed in Table 5 (21), Table 6 shows such an apportionment for an August 1979 aerosol sample from Narragansett. In this sample, the abundances of six of the seven tracer elements were accounted for to better than 20 percent by four of the signatures (NYC gave a negative coefficient, so it was eliminated and the regression was rerun with four sources). The weighting factor in Table 6 is really two factors, one to scale the numerical values of the different elements and another, based on Table 3, to weight As, Se, noncrustal V, and Zn relative to Sb, In, and noncrustal Mn. (The final apportionment is insensitive to weighting factor, however.) Note that about half of the As and Se were associated with the interior signal, whereas 60 to 80 percent of the Sb, Zn, In, and noncrustal Mn and more than 90 percent of the noncrustal V came from the coastal sources. This type of result is common for Narragansett during summer.

Table 7 summarizes the apportionments of 14 consecutive semiweekly

Table 6. Contributions of various source regions to elements in Narragansett aerosol sample GSO 176, 3 to 8 August 1979.

Element	Weighting factor	Concentration (ng m^{-1})					
		NE	BOS	WASH	INT	Total predicted	Observed
As	300	0.03	0.06	0.20	0.36	0.65	0.67
Sb	30	0.08	0.10	0.13	0.13	0.44	0.55
Se	100	0.20	0.13	0.15	0.42	0.90	0.90
Noncrustal V	20	2.20	4.42	1.44	0.80	8.9	9.0
Zn	4	6.11	4.68	3.76	4.31	18.9	18.4
Noncrustal Mn	0.4	1.21	0.53	0.58	1.02	3.34	2.00
In	100	0.0015	0.0006	0.00	0.0015	0.0036	0.0040

Table 7. Least-squares regional coefficients for 14 Narragansett aerosol samples from summer 1979.

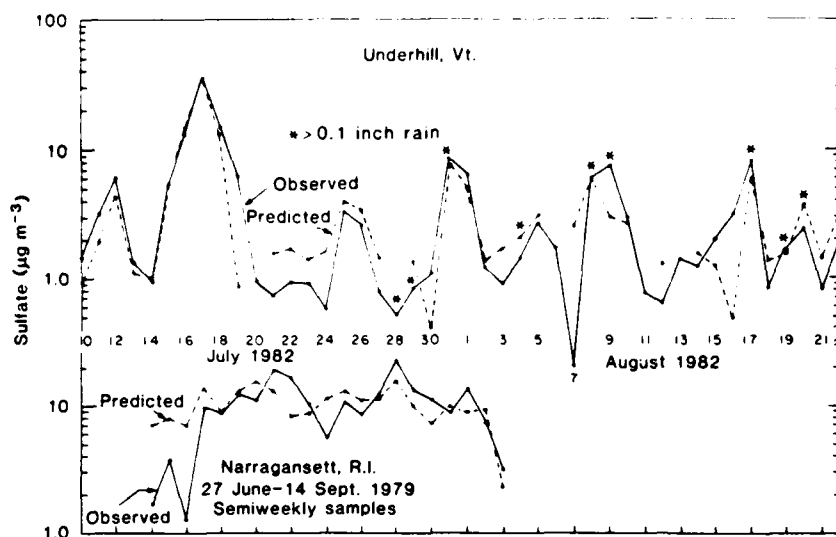| Sample dates	SO$_4^{2-}$ (μg m^{-3})	Regression coefficient				
		NE	BOS	NYC	WASH	INT
13–17 July	8.63	0.66	0.11	0.11	0.02	0.07
17–24 July	12.32	0.37	0.26	0.12	0.01	0.20
24–27 July	11.24	0.00	0.36	0.00	0.00	0.56
27–31 July	19.12	0.00	0.19	0.16	0.00	0.47
31 July–3 August	16.49	0.76	0.00	0.04	0.00	0.34
3–8 August	10.28	0.55	0.13	0.00	0.06	0.24
8–10 August	5.47	0.56	0.08	0.22	0.00	0.23
10–14 August	10.49	0.30	0.37	0.00	0.00	0.19
14–17 August	8.31	1.17	0.07	0.19	0.00	0.00
17–21 August	12.14	0.47	0.35	0.00	0.02	0.00
21–24 August	22.48	0.38	0.47	0.09	0.00	0.00
24–28 August	12.90	0.78	0.17	0.00	0.00	0.16
28–31 August	11.00	0.80	0.05	0.02	0.00	0.14
31 August–4 September	8.71	0.55	0.16	0.00	0.00	0.27

Fig. 2. Observed sulfate at Underhill, Vermont, and Narragansett, Rhode Island, compared to that predicted from least-squares regression of regional signatures.

samples from Narragansett during summer 1979, and shows that the mix of sources can vary strongly in response to large-scale meteorology. During summer 1979, Narragansett had two major sulfate episodes, one in July and one in August. The first was a "typical" summer episode, with winds from the south to west. The second episode was different, however. It had the highest summer sulfate seen to that time in Narragansett but the lowest (most northeastern) noncrustal Mn/V ratios and the lowest As. Meteorological maps showed that this episode was the result of large-scale stagnation in the Northeast of air which had originated largely in the upper Great Lakes and Canada. Thus, the first episode appeared to be mid-Atlantic or interior in origin, whereas the second appeared to be more from New England and Canada.

The apportionments bore out these observations. The first episode had high regression coefficients from the interior, normal coefficients from Boston, and low coefficients from New England. The second episode, by contrast, had zero coefficients from the interior and normal to high coefficients from Boston and New England. Washington aerosol was negligible throughout the period; contributions from the New York area were low to moderate and irregular.

Regional Apportionment of Sulfate Aerosol

Although our tracer system is based on primary pollution elements, that is, those emitted directly as aerosol, an important use of the system will be to understand the regional origins of secondary species, such as sulfate and acidity, which are formed in the atmosphere from primary precursors. Sulfate is the most abundant constituent of many remote aerosols, and both sulfate and acidity are of great concern in acid deposition.

Strictly speaking, primary constituents cannot trace secondary constituents. Near strong sources of (primary) aerosol, such as large urban or industrial areas, our tracer system should work poorly for sulfate. Outside such areas, where regional aerosols dominate, a primary tracer system should work better, although there may still be difficulties. In remote areas, primary tracers should work still better because most of the primary precursors, such as SO_2, will have been converted or otherwise removed; that is, the secondary species will have reached quasi-stable proportions. Under these conditions, the aged regional aerosols would effectively contain a sulfate component linked to the primary signature elements.

This appears to be the situation at Underhill, Vermont, for example. In a series of 39 daily samples from July and August 1982, we determined the "effective" sulfate in the various regional signatures by first apportioning the seven tracer elements, then regressing the sulfate of each sample against the regional coefficients derived for that sample. The results gave the following approximate concentrations of sulfate: 21 ± 1 µg m^{-3} for the interior signature (INT), 7 ± 3 µg m^{-3} for the mid-Atlantic region (WASH), and 3 ± 1 µg m^{-3} for the local aerosol (NE). Based on these values, the

predicted sulfate concentrations generally reproduced the observed values to within ~25 percent (Fig. 2). This accuracy is comparable to that obtained for the primary tracer elements. In particular, each of the peaks and valleys of sulfate was predicted.

At Narragansett, Rhode Island, however, the same approach gave poorer results. Figure 2 shows the observed and predicted sulfate for 21 semiweekly samples during June to September 1979. The fractional errors were twice as large as at Underhill, neither peaks nor valleys were predicted correctly, and a period of low sulfate at the beginning was missed entirely. This behavior is consistent with Narragansett's less remote location and with the abundant SO_2 observed there even during summer (2 to 20 µg m^{-3}) (22). The "noise" in sulfate at Narragansett most likely results from variable and unpredictable oxidation of this subregional SO_2, on a scale too small to be seen at Underhill. Time traces of the elements at Narragansett are considerably more irregular relative to each other and to sulfate than at Underhill. Thus, it appears that both primary and secondary aerosol of the coastal Northeast are more local in origin than those in interior New England and that control of this aerosol and its deposition will require different strategies for different parts of the Northeast.

Future of the Method

The outlook for regional tracers of pollution aerosol is bright. In the 3 years since the first regional tracer was developed, the system has been expanded from two elements to seven and used to demonstrate that characteristic regional signatures are the rule rather than the exception. But the use of regional tracers of pollution aerosol is still new, and nearly every aspect of the procedure is sure to be improved. Particular benefits may come from attention to a few key areas: systematically searching for additional elements with higher tracer power, increasing the statistical validity of regional signatures (including the effects of seasonal and longer period variations in signatures), evaluating the gains from size-segregated sampling, and refining techniques of tracing secondary species such as sulfate and acidity. Incorporation of organic compounds and stable isotopes into signatures should also be beneficial.

Eventually, the ability to follow pollution aerosol over great distances should prove useful in broader areas of the

atmospheric sciences. Applications might include verifying air-mass trajectories on scales at which they cannot be otherwise verified and evaluating large-scale diffusion. A particularly valuable application of elemental tracers should be in determining the source areas of contaminants in precipitation, which is important in the field of acid deposition.

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4. K. A. Rahn, "The chemical composition of the atmospheric aerosol," Technical Report. Graduate School of Oceanography, University of Rhode Island (1976).
5. ———, *Atmos. Environ.* **15**, 1457 (1981). The noncrustal component of an element is used here to mean the mass present in excess of that calculated from a crustal reference element like Al, Si, Fe, or Ti, assumed to be totally crustal in the aerosol (a), and a crustal reference material such as bulk rock or soil (r). The formula typically used to calculate the noncrustal component of element X is

   Noncrustal X_a = total X_a − $Al_a \left(\dfrac{X}{Al} \right)_r$

   In most cases, global mean crustal rock or soil is satisfactory; occasionally, local rock or soil must be used as reference material.
6. The dividing line between fine and coarse aerosol is usually taken to be radius ~ 1 μm. This corresponds to the approximate breakpoint be-
tween (i) particles which penetrate to the lung and those which do not, (ii) coarser particles formed by mechanical subdivision (of soil and seawater, for example) and finer particles formed by coagulation or nucleation, and (iii) the original German "large" and "giant" ranges of particles.
7. Instrumental neutron activation normally allows As, Sb, Se, Zn, and noncrustal V to be determined in replicate aerosol samples to uncertainties of 5 to 15 percent, and In and noncrustal Mn to 10 to 40 percent. Differences between elements in simultaneous samples are usually less than 10 percent; for ratios, most of this difference disappears.
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22. T. R. Fogg, personal communication.
23. We thank N. F. Lewis, K. A. Schweitzer, M. A. Voytek, T. R. Fogg, D. L. Smith, and T. J. Conway for technical assistance. Samples were provided by R. Poirot of the Vermont Agency of Environmental Conservation, C. Brosset of the Swedish Water and Air Pollution Research Laboratory, E. Mészáros and A. Mészáros of the Institute for Atmospheric Physics (Budapest), B. Ottar of the Norwegian Institute for Air Research, R. Kartastenpaa and K. Markkanen of the Finnish Meteorological Institute, and various observers at the GMCC Baseline Observatory in Barrow, Alaska. Samples were analyzed at the Rhode Island Nuclear Science Center. M. Prager performed the calculations involving higher order discriminant analysis. This work was supported in part by ONR contract N00014-76-C-0435, NSF grant DPP 8020928, NOAA grant NA-80-RA-C-0207, a grant from the Ohio Electric Utilities Institute, and the Edison Electric Institute.

105

Who's Polluting the Arctic?

After an eight-year study, a scientist has an answer

by Kenneth A. Rahn

Eight years ago, Glenn Shaw and I began a study of arctic haze, the air pollution that permeates the Arctic every winter from roughly November through April. Although a number of scientists—and some of the public—were aware of this haze, little was known about it. Shaw, an atmospheric physicist at the University of Alaska, had found the arctic air near Barrow, Alaska, to be unusually turbid when he studied it in 1972 and 1974. But the sun photometers that he used to measure turbidity could tell nothing about the composition or sources of the haze or, for that matter, whether it was natural or a byproduct of industrial pollution.

In the years that have followed, we have sampled arctic haze extensively and tried to determine its origins. This effort has taken us to much of the Arctic, as well as to the United Kingdom, eastern and western Europe, and Scandinavia. More recently, scientists from some countries have begun their own efforts to fathom the phenomenon, and so new data continue to come in. But I believe that at this point we can, to some extent, answer our initial questions.

We now know that arctic haze is the result of industrial pollution and that it extends from Alaska eastward at least to Norway, or roughly half the circumference of the Arctic, and probably farther. We know the haze ranges from ground level to at least 18,000 feet and sometimes up to the top of the troposphere (25,000 feet), and that it can be quite dense. We believe it may have numerous environmental effects, including meteorological changes and the pollution of pack ice with heavy metals and organic chemicals.

But perhaps our most interesting finding concerns the origins of arctic haze. During the study, our research group at the University of Rhode Island developed a system of chemical "tracers" that can

reveal where a given sample of polluted arctic air comes from. I have recently reviewed our data, and I am convinced that, due to airflow patterns and other factors, the major source of the pollutants in arctic haze is the Soviet Union. After the Soviet Union, Europe and the United Kingdom are the next largest sources. North America, by contrast, contributes very little pollution to the Arctic, primarily because of airflow patterns and location.

Unlike the Antarctic, the northern polar region is no longer a pristine environ-

ment. In summer its air is clean, but winter brings a reddish brown smog. Not easily visible from the ground, arctic haze probably went unobserved for many years. In the late 1940s, the United States began a series of Alaskan Arctic weather-reconnaissance flights that lasted until the early 1960s. From the very beginning, observers on these "Ptarmigan" flights noticed the haze.

In 1957, J. Murray Mitchell wrote an article reviewing what was known about arctic haze. From direct observation and
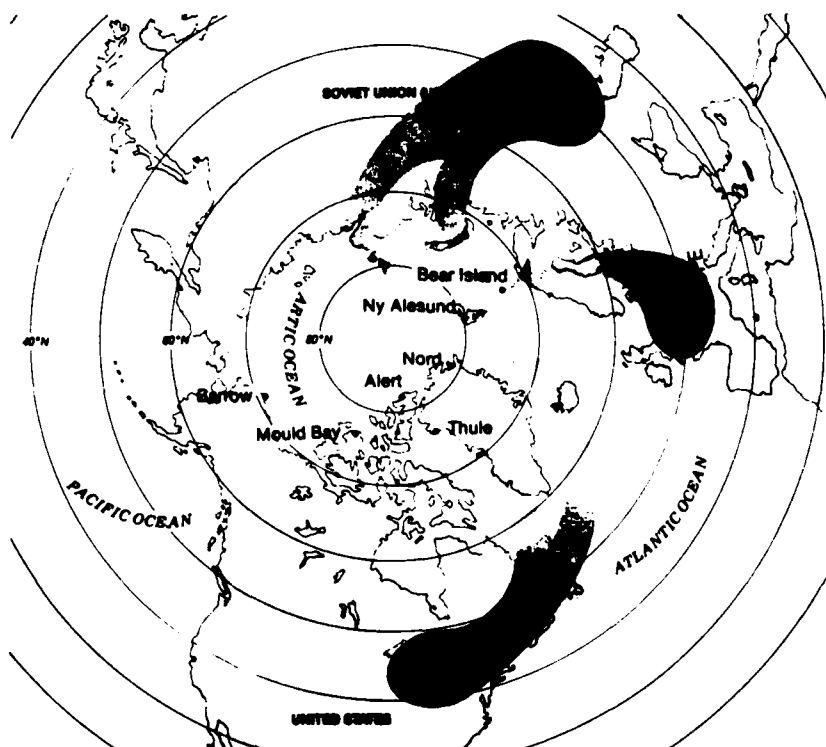
Two airstreams out of the Soviet Union (top arrows) carry most of the pollution that becomes arctic haze. Europe is also an important source of smog (arrow at right). But the northeastern United States (bottom arrows) is not a big contributor to the haze because pollutants are often washed out by storms before they reach the Arctic. The dots represent air sampling stations.

Joe LaMorte

personal interviews with the Ptarmigan observers, he summarized the visual properties of the haze and deduced that it was a true aerosol (fine suspended particles) rather than ice crystals.

Arctic haze was then ignored for fifteen years, until Shaw rediscovered it near Barrow. We began our study in the spring of 1976 when Randolph Borys, now of Colorado State University, took the first aerosol samples. Borys flew in a light plane near Barrow. On some of his last flights, he hit a brief, but intense, period of haze. When we analyzed these samples for trace elements using neutron activation at the Rhode Island Nuclear Science Center, we found that these bands of haze were desert dust from eastern Asia! We were, and still are, impressed that desert dust could have traveled such a long way. For some time afterward, we believed that arctic haze consisted largely of desert dust and was therefore a natural phenomenon. But that fall, a new development forced us to abandon that idea.

In September we had begun to collect aerosol samples at a baseline ground observatory in Barrow operated by the National Oceanic and Atmospheric Administration (NOAA). Our first samples were very light in color and contained little besides sea salt. But about the first of November, the weekly filters suddenly turned dark gray and the concentrations of pollution-derived elements, such as manganese and vanadium, shot up. Vanadium levels increased nearly tenfold. The samples remained this way for months, until the air gradually cleared in late April. By then, we realized that the desert-dust incident had probably been a fluke; arctic aerosol was mostly pollution.

The winter of 1976–77 was one of the most unusual in a century, with extreme cold in the eastern United States and warm weather in lower Alaska. Could the aerosol at Barrow also have been atypical? Samples taken each winter since then have shown that it was not. With slight variations in amount and timing, the dense layer of pollutants has reappeared at Barrow every winter.

At first, there was some disagreement about the source of the aerosol. Shaw and I believed it came from outside the area. Other scientists maintained that it came from Barrow itself or from the North Slope; a few even argued that it consisted of ice crystals or blowing snow. But we knew the pollution could not be of local origin because it contained vanadium, which is produced when heavy oils are burned. Barrow's industries are powered by natural gas and highly refined fuels.

Furthermore, we had set our samplers to exclude aerosol from Barrow.

What puzzled us most at the time was that even given the high levels of vanadium and other pollutants, we still had not found enough pollution to account for the turbidity of Barrow's air. Something was missing. Without much optimism, we began to measure sulfate—the major constituent of most urban air pollution. To our surprise, we found several times more sulfate than expected and easily enough to explain the turbidity. On some days since then, we have gotten sulfate readings in Barrow that are higher than those usually seen in the northeastern United States during winter. The unusual age of arctic pollutants allows more gaseous sulfur dioxide than normal to be converted to particulate sulfate. The discovery of so much sulfate confirmed that we were dealing with a pollution-derived aerosol of distant origin.

Subsequent studies have verified that this is the case. Scientists have detected air pollution in the Canadian Arctic, Greenland, the Norwegian Arctic, and other parts of the Arctic. The haze is truly Arctic-wide. Detailed chemical measurements have revealed that the haze contains every pollution element found at mid-latitudes. Certain organic compounds are also enriched in the arctic atmosphere. Lead 210, a natural radionuclide, reaches record-high concentrations in the Arctic. Pollution gases also accompany the haze. According to R.A. Rasmussen and M. Khalil of the Oregon Graduate Center, methyl chloroform and Freon 22 are the most prominent gaseous tracers of arctic haze.

We were certain that the haze was being imported, but from where? And how did it reach the Arctic? Why was there so much haze in winter but none in other seasons? None of these questions has been answered in detail. But we are beginning to understand how large-scale movements of pollution in the Northern Hemisphere are controlled by the location of land, water, mountains, and human activity.

Scientists usually determine the source of polluted air by calculating its trajectory during the previous few days, using observed winds and pressure patterns. This did not work in the Arctic because of the great distances involved and the paucity of meteorological data. Most major pollution sources are 3,000 to 6,000 miles from Barrow. Using the rule of thumb that air masses move no more than 600 miles a day, we estimate that polluted air takes at least five days to reach Barrow. Air-mass trajectory calculations, however, are not

reliable after about two days. So pure meteorology did not help us locate the sources of pollutants.

Next we considered indirect and circumstantial evidence. North America seemed an unlikely source region because the major airstreams to the Arctic, northward along both sides of Greenland, were on a storm track that washed out pollutants. We eventually confirmed this by taking direct measurements on Iceland. These showed that the pollution there came from Europe, not North America. The western airstream to the Arctic was harder to evaluate. Eastern Asia (Japan, Korea, China) seemed an unlikely source because its air travels across the Pacific Ocean and up the Bering Strait and arrives in Barrow very clean. This left only Europe and central Asia.

Eurasian sources were favored because they are located at least ten degrees of latitude (600 miles) farther north than sources in North America or eastern Asia. Available data from northern Europe indicated that a tongue of high sulfate concentrations extended into the Norwegian Arctic. We also knew that pollution often reached northern Scandinavia by flowing north from central Europe in an airstream between Atlantic low-pressure and Eurasian high-pressure masses. A slight northward extension of this stream would carry pollutants to the Norwegian Arctic and from there over the pole to Barrow.

But these were only *our* thoughts. As other atmospheric scientists became interested in arctic pollution, they offered new suggestions about its possible origin and transport. When NOAA researchers analyzed several years' data of five-day back trajectories from Barrow, they found that air came to the Arctic from all conceivable directions; potential sources of pollution could not be distinguished. Another study correlated flow patterns in the mid-troposphere (18,000 feet) with periods of greatest pollution levels at Barrow and strongly implicated New England, via an airstream over the North Atlantic. But European sources could not be eliminated because air from Europe could have traveled along the same path.

Many more theories were proposed. Scientists who calculated the forward trajectories of winds at 5,000 feet predicted that North America and Europe should contribute equally to arctic haze. One researcher used the positions of the polar front in winter to conclude that Asia was the most important source. Others argued that pollution from all parts of the globe mixed in the upper troposphere or lower stratosphere before settling down in the

Arctic. At various points, arctic haze was blamed on a smelter in Ontario, copper and nickel smelters at Noril'sk in the northern Soviet Union, and swamps in Alaska.

Clearly, we needed a new approach to determine the sources and transport of arctic pollution. For some time we had felt that our best chance for success lay in detailed chemical analysis of the aerosol itself. If we could find systematic chemical differences in the polluted air from various sources and if these differences were preserved during the long journey to the Arctic, we would have a powerful interpretive tool.

What we were looking for were regional signatures, which had never been found to exist. The regions that contribute to arctic haze are large and they all produce all types of pollution. Available analyses showed that the similarities were greater than the differences. Furthermore, we didn't know how to go about constructing a regional signature or even what elements to use as tracers. Lastly, we needed large amounts of data from widespread regions to develop what we wanted. Little or no such data existed.

By late 1979 we had nearly given up looking for regional differences, but in April 1980 a conversation I had with L.A. Barrie, of Environment Canada, sparked a new approach. We had both lived and worked in Europe and had noted that the levels of manganese there were much higher than in North America. The opposite was true for vanadium levels. This prompted me to try to construct a tracer using the ratio of manganese to vanadium. In principle, the ratio of two elements might vary considerably and have distinct advantages as a tracer, because the combined value should change much more slowly during transport than the concentration of either element alone.

That is exactly what we found. The ratio of manganese to vanadium was five times higher in western Europe than in eastern North America. The ratio in the Norwegian Arctic was half that of the North American Arctic. For the first time, we could talk about regional differences. Our data from the Norwegian Arctic seemed to show that haze there came from Europe. But the relatively high manganese–vanadium ratio in the North American Arctic didn't seem to match European *or* North American sources. It had to come from a place whose pollution was unlike any we had seen.

Spurred on by the promise of the manganese–vanadium ratio, my research group at Rhode Island and I began to look

for other signatures. We considered some twenty elements because they are pollution-derived and can be measured by neutron activation. Eventually seven elements—arsenic, selenium, antimony, zinc, indium, manganese, and vanadium—became the basis for our current tracer system. By setting up six ratios to selenium, we obtained a series of values that is a more reliable guide to a region's air pollution.

Recently I realized that natural selenium in the Arctic might be distorting our numbers, so we substituted antimony in the denominator of our ratios. With these values, we have identified at least fifteen distinct regional signatures in Europe and North America. These signatures are maintained for thousands of miles.

Now we can trace the origins of arctic haze. In the Norwegian Arctic, the pollution often comes from the United Kingdom and Europe, associated with airflow from the west and south. But about half the time, a different signature is present, one that is hard to mistake because of its very high ratio of arsenic to antimony. Since the air masses bearing this signature come from the east and south, typically moving counterclockwise around large low-pressure areas centered near Novaya Zemlya, I believe their aerosol originated in the central Soviet Union. Arctic haze near North America is generally similar: about half of it has a Soviet Union signature. Most of the other signatures are from Europe and the United Kingdom, with an occasional pulse from North America.

We had suspected the Soviet Union might be the key source of Barrow's haze ever since our original readings there showed a high manganese–vanadium ratio. Although we don't yet know the exact region of origin within the Soviet Union, the likeliest possibility is the industrialized southern Urals. The economy of the region is based on coal, and the area is full of steel mills and nonferrous smelters. It has some of the highest pollution levels in the entire Soviet Union. We have not been able to take air samples in the central Soviet Union, but the U.S. government, which makes routine flights over the Arctic, has provided us with samples of aerosol that has come to the Arctic from that area. Its signature matches what we found in the rest of the Arctic. I have analyzed these data, and I believe that the Soviet contribution to arctic haze on its own side of the Arctic may be as high as 70 percent.

Our regional tracers show that Eurasia is the major source of arctic haze, that airstreams transport the pollutants directly to the Arctic via the lower troposphere,

and that the pollutants from Eurasia and North America do not mix much before arriving at the Arctic.

Because we now know the precise geographic sources of the pollution, we can deduce which meteorological mechanisms control its transport. Generally, low-pressure and high-pressure masses act together. In Eurasia, lows from the Atlantic Ocean follow the warm water around the top of Scandinavia. The highs, usually variants of the Asiatic high, can be centered anywhere in Eurasia. While still over the Atlantic, the low draws aerosol from central Europe into the Norwegian Arctic. Once the low passes north of Scandinavia, however, it weakens and rarely gets beyond Novaya Zemlya. The combination of the low over Novaya Zemlya and the Asiatic high produces a strong northward airflow, centered on the eastern Taymyr peninsula. This is probably the most important pathway for Soviet pollution into the Arctic.

North America is not a major source of pollution to the Arctic for several reasons. Because the continent is smaller, its high-pressure areas are weaker than those of Asia. North American highs move southeastward to the Atlantic. In addition, low-pressure areas approaching western North America are broken up by the Rocky Mountains so they do not interact strongly with North American highs. The situation is completely different in Eurasia. First, European mountains are not big enough to break up the Atlantic lows. The highs over Asia, however, are held in place by mountains to the east and south—for example, the Yablonovyy, Khingan, Stanovoy, and Dzhugdzhur ranges, and the Himalayas. The result is that Atlantic lows easily link up with the Asiatic high and create a zone of strong northward airflow. Because the Eurasian pressure systems are farther north and more inland than their North American equivalents, they contain less moisture and wash out pollution less effectively. These meteorological factors, combined with the northerly placement of cities and industry, make Eurasia the greatest source of arctic haze.

Why is arctic haze only a feature of winter? There are several reasons. First, the stable winter air of Eurasia allows more pollutants to build up. Second, the vigorous airflow patterns of winter draw in pollutants. Finally, because precipitation in the Arctic during winter is slight, little pollution gets washed out of the air.

We still have much to learn about the environmental effects of arctic pollution, but we know the basic dynamics. Aerosol

108

particles in the atmosphere scatter and absorb visible light, which can alter the heat balance. Arctic haze is unusually rich in sooty carbon, which absorbs light reflected off the pack ice and heats the haze layers to an unusual degree. Several studies, most recently by F. Valero and associates at NASA's Ames Research Center in California, have shown that black carbon could warm the Arctic during spring. Since other researchers have already predicted a worldwide warming trend because of increased carbon dioxide levels, the effect could be intensified in the Arctic at that time of the year.

Although there are those who disagree, I don't believe we need to worry that the Arctic icecap will melt. For one thing, the maximum warming from carbon should occur well above the surface of the pack ice. The surface itself should actually be cooled. Also, the lifetime of aerosol particles in the haze is short—days or weeks—and this means that the haze each year comes exclusively from that year's emissions. By contrast, carbon dioxide remains in the atmosphere for a decade or more, and thus its deleterious effects are constantly compounded.

Arctic haze may have indirect effects on heat balance. For example, the reflective properties of clouds that form in hazy air may be altered. Also, sooty snow on the pack ice may absorb light. This could extend the warming effect of black carbon into the summer, when the Arctic gets the most sun. While potentially very important, this effect has not been studied in any detail.

Another major environmental impact of air pollution stems from the formation of cloud droplets and ice crystals around aerosol particles. This could affect how efficiently clouds can form, their radiative properties, or the amount of precipitation from them. The first study in this area, a doctoral thesis by Randolph Borys, shows that arctic haze increases cloud-condensation nuclei but reduces ice nuclei. The increase can be attributed to sulfate in the air but the decrease in ice nuclei is unexplained. Borys is continuing his study.

Still less is known about how the deposition of heavy metals, organics, and other chemicals is affecting the pack ice. Some years ago, I calculated that the arctic atmosphere is probably the greatest source of lead to the Arctic Ocean. Beyond this, little work has been done on deposition, and no formal work has been done on its effects on wildlife.

One of our greatest disappointments has been the Soviet Union's lack of cooperation in the international study of arctic haze, despite repeated overtures to various individuals and institutions. However, interest is growing in other countries. Last spring, for example, five research aircraft—from West Germany, Norway, and the United States—sampled air in the Arctic. The first results from these campaigns are just beginning to appear, with a great deal of new information. Observers saw multiple bands of concentrated pollutants, but outside these bands, the air was clean. They also found horizontal ducts of pollution close to clean high-pressure areas whose air seemed to be carried in from above. The effects of pollution from individual towns appeared to be limited.

Another set of aircraft studies is already being planned. The Norwegian Institute for Air Research is conducting an intensive five-year study of the Norwegian Arctic from multiple ground sites, as well as aircraft. Canada will be looking at the problem more intensively, too, and this month the Third Symposium on Arctic Air Chemistry will be held in Toronto. Out of all this activity should come a clearer understanding of this intriguing and troubling phenomenon.

PROGRESS IN ARCTIC AIR CHEMISTRY, 1980–1984

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ARCTIC AIR CHEMISTRY IN 1980

The Second Symposium on Arctic Air Chemistry was held at the University of Rhode Island, 6–8 May 1980. At that time, Arctic air chemistry was known to only a few researchers whose disciplines were directly related to it. Large-scale pollution of the Arctic winter atmosphere by particles and gases transported up to 10,000 km from midlatitude industrialized areas, the most striking example of routine long-range transport of air pollution known today, had not yet reached the collective consciousness of scientist or layman. Arctic haze was not the household word that it is today. More questions than answers remained, more doubts than certainties. Twenty-one papers from the Second Symposium were published in a special August 1981 issue of *Atmospheric Environment* (Volume 15, No. 8). This publication, with the attention it drew to the field, began a new era for Arctic air chemistry.

The participants in the Second Symposium generally agreed on the following aspects of Arctic air chemistry:

The entire Arctic is polluted during winter. Sources within the Arctic are generally unimportant regionally, although they can be significant on a smaller scale.

The Arctic aerosol contains a huge variety of constituents, including metals, sulfate, graphite, silicones and organics.

The dominant constituents of Arctic pollution aerosol during winter are nonmarine sulfate ($2 \mu g \ m^{-3}$), organics ($1 \mu g \ m^{-3}$), and soot ($0.3-0.5 \mu g \ m^{-3}$).

Statistical techniques such as factor analysis show promise for understanding the sources of the aerosol.

Many other aspects of Arctic air chemistry were not fully understood, however, because of incomplete or conflicting data:

Other than the original optical observations by Mitchell (1957), little or no quantitative vertical data on Arctic haze were available.

While pollution gases were considered certain to accompany the haze aerosol from midlatitudes to the Arctic, SO_2 data were only available for Bear Island, and few other potential gaseous tracers of Arctic haze had been measured anywhere in the Arctic.

Major disagreements about the sources and transport of Arctic haze existed. In the course of the Symposium, arguments were presented for the major

sources being in New England and Europe (based on planetary waves), in Europe and the U.S.S.R. (based on the Mn/V ratio), from various continents (based on Monte Carlo techniques), and on all midlatitude sources (based on eddy-diffusion theory).

The main altitude of transport could only be guessed at (below 3 km).

The basic character of the transport was not agreed upon. While most felt that it was organized, some favored diffusive transport.

Two principal pathways from Eurasia to the Arctic were proposed but not rigorously verified: an anti-cyclonic pathway from Europe and a cyclonic pathway ('return-flow') from Europe and the U.S.S.R. via the Taymyr Peninsula.

The nature of the polluted Arctic airmass was also debated. Some felt that it was a stable reservoir with a relatively long residence time of air, which receives small pulses of polluted air from one side and releases small pulses of mixed air elsewhere. Others proposed that parcels of polluted air pass through the Arctic faster and more intact.

Although back-trajectories to potential source areas were discussed at length, and their importance agreed upon, they could not be used to pinpoint specific source areas, even to the point of distinguishing N America from Eurasia.

Little new about the radiative effects of Arctic aerosol was offered beyond the original estimates of Shaw and Stamnes (1980). It was generally agreed, however, that Arctic aerosol heats the local atmosphere during spring, that heating rates could be large, and that this topic should be pursued.

Only one study of potential nucleational effects of Arctic haze was in progress (R.D. Borys, Colorado State University).

Little was known about sinks of Arctic haze, other than the general observation that removal rates in the Arctic had to be slow to explain the high concentrations of haze.

EVENTS DURING 1980–1984

At the time of the Second Symposium, Arctic air chemistry seemed on the threshold of developing into a fully-fledged discipline. Subsequent events bore this

out. If anything, the field progressed and broadened faster than anticipated. The few scientists working with meager budgets at isolated facilities in the Arctic were replaced by larger and more comprehensive programs with field sites at many more locations in the N American and European sectors of the Arctic. The 5-y study of air quality in the Norwegian Arctic by the Norwegian Institute for Air Research was an example of the new type of program. In addition, the American NOAA (National Oceanic and Atmospheric Administration) and the Canadian AES (Atmospheric Environment Service) intensified their work in the N American Arctic.

Aircraft studies arrived in force as well. In Spring 1983, no fewer than five research aricraft flew in the vicinity of Alaska, Greenland and Norway. The most extensive of these programs, the NOAA AGASP (Arctic Gas and Aerosol Sampling Program) experiment, was the focus of a feature article in *Environmental Science and Technology* (Hileman, 1983) which also discussed the background to the project. The May 1984 issue of *Geophysical Research Letters* (Vol. 11, No. 5) contained 29 papers on AGASP and related studies of Arctic haze. A popular article on Arctic haze appeared in the May 1984 issue of *Natural History* magazine (Rahn, 1984). All in all, then, Arctic air chemistry had a significantly higher profile than ever before.

PROGRESS IN UNDERSTANDING ARCTIC AIR CHEMISTRY

But what about the science? Did all this activity open new areas of research within Arctic air chemistry, or resolve any of its longstanding debates? The answer to both questions is affirmative, although many areas remained to be explored and developed.

Horizontal and vertical distributions of Arctic haze

Consider first some of the successes. The aircraft experiments rapidly opened up the third dimension of Arctic air chemistry. Arctic aerosols and gases were sampled up to the tropopause and occasionally above. Horizontal and vertical structure (bands and patches) was found everywhere. Some types of structure, such as well-defined transport zones, were linked to large-scale meteorology, whereas others (horizontal patchiness, for example) were not. As a result of these aircraft experiments, we may no longer view Arctic haze as a uniform blob covering the entire Arctic at any one time. Only in the long term is the haze distributed quasi-uniformly.

The intensity of vertical and horizontal structure in the Arctic atmosphere is striking. Within a narrow haze band, concentrations of pollutants can easily exceed those outside by an order of magnitude. The vertical separation between clean and dirty air can be as little as 100 m. Horizontal variations, while not so sharp, are still surprisingly distinct: while flying level,

the AGASP P-3 constantly flew in and out of patches on a time scale of 30 min or less. On one flight in the Norwegian Arctic, the aircraft encountered an unexpected 'aerosol front' and passed from dirty air to clean air in just a few minutes (Raatz and Schnell, 1984).

No uniform top to the haze was found. The visual layers tended to become much less abundant and intense above 600 mb, but there were exceptions. Black carbon was found up to the tropopause (Rosen and Hansen, 1984). While haze was universally found below the top of the surface inversion, it was often less intense than that higher up, and may have been moving more slowly as well. Although the most rapid transport of haze was sometimes found aloft (Radke *et al.*, 1984a), significant transport within the inversion layer could not be excluded.

Sources and transport of Arctic haze

Quite independent of these aircraft experiments, considerable progress was made in understanding sources and transport of Arctic haze. Heidam (1984) used factor analysis of elemental data from Greenland to deduce that pollution aerosol there had at most three components: combustion, metallic and automotive. The metallic factor seemed to originate with emissions in the Urals; the other factors did not seem to come from any particular area.

Raatz and Shaw (1984) used Mn and V data from Barrow aerosol to infer source regions and construct a series of principal synoptic configurations and transport pathways from N America, Europe and Asia to that site which appeared to be consistent with the elemental data. This was a remarkable achievement, both because it was a purely synoptic exercise with its two end points controlled by chemistry, and because many of its results were subsequently confirmed during the AGASP flights.

Simultaneously, considerable effort was expended to construct state-of-the-art trajectories for Arctic haze events in general and the AGASP period in particular (Harris, 1984). When all the information on sources and transport was considered, it became clear that the quality and reliability of trajectories had improved considerably, even if they were not quite ready to stand on their own.

Perhaps the most significant advance in our understanding of sources of Arctic haze was to recognize that the Soviet Union is one of the major contributors to Arctic air pollution. This conclusion was the product of chemical and meteorological evidence alike. Ironically, however, the role of the U.S.S.R. was accepted almost *too* uncritically, at least in the opinion of this writer. At the time of the Second Symposium, the first pieces of chemical and meteorological evidence pointing to the Soviet Union were beginning to appear (Rahn, 1981a; Rahn, 1981b; Barrie *et al.*, 1981; Heidam, 1981; Carlson, 1981). They were suggestive but not definitive. Next, Shaw (1982) used the chemical

and meteorological characteristics of three strong haze episodes in central Alaska during February-April 1982 as the basis for proposing that the Noril'sk smelting complex in the north-central U.S.S.R. could be a very important source of Arctic haze. Rahn *et al.* (1983) felt that this was an overstatement, however, and countered with several lines of evidence that Noril'sk could account for no more than one-tenth the sulfate seen at Barrow, and that the central Soviet Union as a whole, or some comparable source area, was required to pollute the entire Arctic air mass.

Opinion on the importance of the U.S.S.R. as a source was further molded by the AGASP experiment of March and April 1983, during which an abnormal circulation pattern brought haze to the Alaskan and Norwegian sectors of the Arctic persistently from the direction of the central U.S.S.R. When considered critically, however, much of the preliminary AGASP evidence is considerably weaker and more ambiguous than originally supposed, although not necessarily wrong. In international matters like this, one must be extremely careful not to assign responsibility for environmental degradation until the case is beyond reproach.

Environmental effects of Arctic haze

The sense of the high heating rates calculated originally by Shaw and Stamnes (1980) was confirmed but placed in perspective. Extensive additional measurements of carbon in the Arctic, its absorption of light and radiative calculations showed that heating rates comparable to the 1°C per day estimated by Shaw and Stamnes from indirect evidence can certainly be found in the Arctic during spring, particularly in zones of intense haze extending well into the free troposphere (Porch and MacCracken, 1982; Cess, 1983; Valero *et al.*, 1984; Rosen and Hansen, 1984; for example). Lower concentrations of black carbon, smaller absorption of light per unit mass, and less vertical extent than previously supposed may cause average heating rates in spring to be well below 1°C per day, perhaps as low as 0.01-0.1°C per day, and thus of debatable environmental importance (data and conclusions from Heintzenberg, 1982; Mendonca *et al.*, 1982; Patterson *et al.*, 1982; Freund, 1983, Clarke *et al.*, 1984). Even though black carbon is found throughout the Arctic atmosphere in winter, absorbs sunlight strongly, and warms the layer of air in which it is found, the degree of warming appears to be small enough to allay environmental concerns.

Our understanding of other environmental effects of Arctic haze did not progress so rapidly, though. Borys found that Arctic air containing haze nucleates cloud droplets much more effectively than does Arctic air without haze, but that air with haze actually nucleates ice crystals less effectively than air without haze (Borys, 1983). The positive condensation-nucleus effect is probably caused by the abundant sulfate particles in the Arctic; the reason for the negative ice-nucleus effect

is still unknown. Much work remains to be done on nucleational effects of Arctic haze: we still do not know whether Arctic haze changes the frequency of clouds in the Arctic, their amount, their microstructure, their radiative properties, or the amount of precipitation from them.

Depositional effects of Arctic haze were similarly unstudied. We still do not have systematic data on the rate at which contaminants are removed from the Arctic atmosphere or whether any of them are fractionated as they are removed. We can only guess at the fraction of Arctic haze which is removed in the Arctic (a very rough figure of one-third of the sulfate would seem to be consistent with available data) or what fraction returns to midlatitudes. Arctic haze has not yet been observed re-entering midlatitudes.

Particle-size distributions

The particle-size distributions of Arctic aerosol are of considerable interest. At the time of the Second Symposium, there were essentially no direct measurements available, and it was assumed that the haze was nearly exclusively limited to the 'accumulation' mode between radii of 0.1 and 1 μm. During 1980-1984, new data showed that most of the mass is indeed in that range, but that more than expected is found at larger and smaller particle sizes. All studies, including for example those of Heintzenberg (1980) and Shaw (1984), have found the great majority of the Arctic aerosol's mass to be in or near the accumulation mode. During strong episodes of transport to the Arctic, this size range is characteristically enriched relative to other times (Pacyna *et al.*, 1984; Shaw, 1985; Lewis, 1985). Shaw (1983), however, found that aerosol during haze periods outside Fairbanks, Alaska has high enough concentrations of extremely fine particles (radius roughly 0.03 μm) to indicate that they must still be formed actively during the polar night.

At the other end of the spectrum, there is now abundant evidence that the Arctic aerosol is less depleted in coarse particles than previously supposed: (a) Heintzenberg *et al.* (1981) measured the coarse and fine fractions of 17 constituents at Spitsbergen during late winter 1979, and found that the results resembled a well-aged pollution aerosol from midlatitudes, i.e. most of the Fe, Si, K, etc. was coarse-particle whereas most of the Pb, Zn, Cu, sulfate, etc. was fine-particle; (b) six subsequent reports have confirmed that haze aerosol contains considerable coarse-particle (super μm) mass: Hoff *et al.* (1983) and Leaitch *et al.* (1984) for the Canadian Arctic, Pacyna *et al.* (1984) for the Norwegian Arctic, Lewis (1985) for the surface at Barrow, and Bailey *et al.* (1984) and Radke *et al.* (1984b) for haze bands aloft near Barrow.

Bromine in the Arctic atmosphere

One of the more bizarre aspects of Arctic air chemistry is the unusually high particulate and gaseous bromine found near the surface from mid-February through to mid-May (Berg *et al.*, 1983). During this

112

period, the bromine concentrations in the Arctic troposphere are the highest of any nonurban area in the world. Berg *et al.* (1984) found that concentrations of bromoform could reach 46 pptv and accounted for 38 % of the gaseous Br; Rasmussen and Khalil (1984), however, suggested that total gaseous Br during spring was only 10 % greater than during the rest of the year. Although the Arctic Ocean is the most likely source of excess springtime bromine, other sources, including long-range transport of pollution, have not been ruled out completely. Bromine in the Arctic atmosphere is clearly worthy of further study.

Trace gases in the Arctic

During 1980–1984, it became clear that pollution gases accompany Arctic haze. 'Arctic haze' should now be considered a generic term for generally polluted air masses in the Arctic, not just their particulate component. The work of R. Rasmussen and M. Khalil (Khalil and Rasmussen, 1983; Rasmussen *et al.*, 1983; Khalil and Rasmussen, 1984; Rasmussen and Khalil, 1984; for example) showed that a large group of these gases, of which methyl chloroform and Freon-22 are good examples, have pronounced seasonal cycles in phase with the haze aerosol and thus can serve as gaseous tracers. Other gases, with longer half-lives and smaller cycles, are less effective tracers even though they may be just as pollution-derived. Oehme and co-workers (Oehme, 1982; Oehme and Stray, 1982; Oehme, 1983) used gas chromatography and negative-ion chemical ionization mass spectrometry to detect various gaseous hydrocarbons and chlorinated hydro-carbons in the Norwegian Arctic and to show that they hold promise as tracers, even during summer when aerosol tracers are not useful. Gaseous tracers seem to be sufficiently valuable that they should be investigated and exploited to the fullest.

Historical aspects

The history of Arctic haze is one of its most important aspects. Because systematic air samples were not taken in the Arctic before 1976, historical information has to come from ice cores. Until recently, the only cores available were from Greenland, which is too elevated (nearly 10,000 ft) to respond to the bulk of Arctic haze. Koerner and Fisher (1982), however, used cores from Ellesmere Island to show that hydrogen-ion deposition began to increase from about 1950 and continued at about 5 % per year. Thus, Arctic haze is at least partly a post-war phenomenon. Ice-core studies like this should be continued. Analysis of trace elements with smaller natural backgrounds than acidity should allow the history of Arctic haze to be written even more clearly.

Cooperation with the Soviet Union

Perhaps the biggest disappointment of 1980–1984 was the lack of cooperation by the Soviet Union. The U.S.S.R.'s State Committee on Hydrometeorology and Protection of the Natural Environment was invited

twice to attend the last two Symposia, and did not reply to any of these overtures. Cooperative studies in the Arctic have been repeatedly proposed via the U.S.-U.S.S.R. Bilateral Agreement on Cooperation in the Field of Environmental Protection and declined by the U.S.S.R. In view of the U.S.S.R.'s role as a major source of Arctic air pollution, this stance is most regrettable. The contribution of the U.S.S.R. to Arctic air pollution will apparently have to be determined without them.

THE THIRD SYMPOSIUM ON ARCTIC AIR CHEMISTRY

The Third Symposium on Arctic Air Chemistry was held at the Atmospheric Environment Service in Downsview, Ontario, Canada, 7–9 May 1984. Of the 31 papers presented there, 15 are represented in this issue, supplemented by eight closely related papers. The talks covered nearly all aspects of Arctic air chemistry, and included:

N American, Greenland and Norwegian sectors of the Arctic;
chemical, physical and radiative properties of the aerosol;
gaseous and particulate pollutants;
surface and aircraft measurements;
meteorological aspects of Arctic air pollution;
the history of Arctic haze.

The rest of this section presents selected highlights of the Symposium and the papers published here, and represents the impressions gained by this writer only.

Horizontal and vertical distributions

Of the 11 papers in this issue derived wholly or in part from aircraft studies, 10 come from NOAA's AGASP. A number of these papers expand upon earlier versions published in the May 1984 *Geophysical Research Letters.* Raatz *et al.* (1985a) and Raatz *et al.* (1985b) present the horizontal and vertical distributions of Arctic haze in the Norwegian and N American sectors of the Arctic, and relate their findings to synoptic configurations. Wendling *et al.* (1985) show that the black carbon in the Norwegian Arctic was mostly confined to the lowest kilometer during spring 1983. Conway *et al.* (1985) report that CO_2 concentrations aloft varied by several ppm, depending on the proportions of clean and polluted air. Hansen and Rosen (1985) found considerable horizontal varia-tions of black carbon; some correlated with meteoro-logical features but others, on the scale of 50–100 km, did not. Winchester *et al.* (1985) found particulate Cl enriched near the surface and maximum particulate S within a tropopause fold.

Sources and transport of Arctic haze

Sources. In the first detailed application of their seven-element tracer system to the Arctic, Lowenthal and Rahn (1985) confirm that Eurasia was the domin-

ant source of aerosol to Barrow during winter 1979-80: only 5-10% of the aerosol could be attributed to N American sources. Within Eurasia, the central Soviet Union contributed about 50% of the sulfate and 75% of most of the tracer elements, with the remainder coming from Europe.

Two papers deal with sources of pollution aerosol in Greenland: Davidson et al. (1985) present some of the first evidence that Dye 3 receives material from Eurasia transported over the Pole in the same manner found for more northern Arctic sites, and Heidam (1985) uses crustal enrichment factors and synoptic maps to argue that combustion products are transported episodically from N America and Europe, whereas metals come primarily from the Urals. Pacyna and Ottar (1985) use elemental concentrations and trajectories for the Norwegian Arctic in summer 1983 to define episodes arriving from N America, Greenland, Europe and the Soviet Union.

Sheridan and Musselman (1985) measured the chemical composition of 800 sub μm and 516 super μm particles from the AGASP flights in the Alaskan Arctic. The sub μm particles were nearly all sulfuric acid. The coarser particles included graphitic carbon, coal and oil fly ash, and Pb–Zn–Cu from nonferrous smelting, and were often linked to trajectories from industrialized parts of the Soviet Union.

At a more general level, Graustein and Barrie (1985) use abundances of ^{210}Pb, sulfate, Mn and V at Mould Bay to confirm the continental influence on the Arctic atmosphere during winter and to argue that the effect of pollution sources south of 60 N is limited to January and February. On the other hand, Rosen and Hansen (1985) used calculated fluxes of particulate sulfur and black carbon to the Arctic as the basis to contend that pollution sources south of 60 N control the abundances of these elements in the Arctic throughout the winter.

Transport. In five papers, the NOAA/GMCC group probes further into the meteorological aspects of transport of Arctic haze during AGASP. Raatz (1985) uses detailed synoptic analysis to argue that the episode of Arctic haze observed at Barrow during March 1983 originated first from the Volga–Urals region, then from central/eastern Europe. Raatz et al. (1985c) found that the strongest haze at Barrow appeared in a transport zone along the eastern side of the Arctic anticyclone. Raatz et al. (1985a) noted the maximum haze in the Norwegian Arctic in transport zones associated with return-flow systems. The maximum of transport was between 600 and 800 mb, in a zone 250–350 km wide, and with wind speeds of 8–10 m s^{-1}. Raatz et al. (1985b) stressed the importance of transport zones for explaining the maximum haze near the Pole. Intrusions of stratospheric air into the Arctic troposphere were reported by Raatz et al. (1985b) and Raatz et al. (1985d).

Iversen and Joranger (1985) proposed that blocking controlled the transport of pollutants from Eurasia to the Norwegian Arctic.

Environmental effects of Arctic haze

Both radiative and depositional effects of Arctic haze are reported here. Absorption of visible light by the aerosol in central Alaska is approximately half that in the high Arctic (Shaw, 1985). In the Norwegian Arctic, maximum heating rates due to Arctic aerosol are calculated to be approximately 0.1–0.15 K per day (Wendling et al., 1985), in close agreement with Porch and MacCracken (1982) and considerably lower than others reported previously. Clearly, the long-term radiative effects of Arctic haze are not yet agreed upon.

Studies of deposition of trace elements in Greenland reported by Davidson et al. (1985) have found both relatively low deposition velocities (0.1–2.5 cm s^{-1}) and clear evidence for the order-of-magnitude fractionation between coarse- and fine-particle elements proposed for Barrow from much less systematic data by Rahn and McCaffrey (1979). In northern Greenland, dry deposition may account for more than 30% of the total.

In a new kind of study, Clarke and Noone (1985) have found that black carbon is present in Arctic snow in amounts consistent with atmospheric abundances and common washout ratios for sub μm aerosol. These concentrations in snow are enough to reduce its albedo by 1–3% in fresh snow and 3–10% in aged snow. This radiative effect on the Arctic should be investigated further.

Particle-size distributions

Four additional reports are now available on particle-size distributions of the Arctic aerosol or its individual components: Shaw (1985), Barrie and Hoff (1985), Lewis (1985), and Winchester et al. (1985). All agree that the major mass, either measured directly or inferred via sulfate, is sub μm. The last three, however, show that substantial mass is also present in the super μm range. This agrees with the sense of the earlier results discussed above. In addition, Shaw (1985) finds that both the mass of accumulation-mode aerosol and the mean size of the total aerosol of interior Alaska increase with decreasing temperature during winter, and speculates that a temperature-dependent condensation mechanism might be responsible.

Bromine in the Arctic atmosphere

Barrie and Hoff (1985) report similar concentrations and seasonal variations of particulate Br at Mould Bay as found earlier for Barrow by Berg et al. (1983). Barrie and Hoff note that uptake of reactive gaseous Br by cellulose and Nuclepore filters has not been ruled out, however.

CO$_2$ in the Arctic

Our understanding of CO$_2$ in the Arctic atmosphere continues to increase. Higuchi and Daggupaty (1985) show that anomalies of CO$_2$ at Alert are similar to those at Barrow in that summer maxima and minima

are associated with flow from southern and northern latitudes, respectively, whereas in winter the reverse holds. Another interesting aspect of CO_2 in the Arctic is the pulses observed at Barrow during winter and spring (Peterson et al., 1982, for example). By using nonmarine sulfate and noncrustal vanadium as indicators of pollution aerosol, Halter et al. (1985) related the pulses of CO_2 during winter 1979-80 to direct transport of industrial emissions from Eurasia. To the best of our knowledge, this is the first time that CO_2 in such a remote area has been associated with transport from polluted areas.

Historical aspects

Barrie et al. (1985) have extended the original historical study of Koerner and Fisher (1982) on deposition of acidity to Canadian glaciers by showing that annual maximum conductivity is the best indicator of Arctic air pollution and that the apparent 75% increase in Arctic air pollution between 1952 and 1977 nearly matches a doubling of SO_2 emission in Europe.

THE FUTURE

The future of studies of Arctic air chemistry is generally bright. Arctic haze is now known much more widely than it was a few years ago, and is generally recognized as an area worthy of study, both for what can be learned about the Arctic and for what can be learned about transport and aging in general. The Arctic offers a natural laboratory in which coherent air masses can be followed over much longer distances and greater times than in midlatitudes: 10,000 km and 10 days are not uncommon. Large, high-profile studies like AGASP have created considerable momentum which should assure the future of Arctic studies for the next several years.

There are other optimistic signs as well. The Arctic Research and Policy Act of 1984 passed by the U.S. Congress has, for the first time, given Arctic research a formal status akin to that traditionally held by Antarctic research. It is gratifying to know that the Arctic will no longer be the stepchild that it once was. The Antarctic is clean and pure, pristine and noble. Its giant land mass serves as a natural focus for attention and activities. By contrast, the Arctic is indeterminate, broken up and dirty. The Antarctic represents the pristine character that civilization has lost and dreams of somehow regaining. The Arctic is what we as an industrialized hemisphere have really become; it mirrors our societal faults. Thanks to Senator Frank Murkowski of Alaska, the desirability and importance of Arctic research and policy are now also recognized officially, at least in the United States.

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REGIONAL SOURCES OF POLLUTION AEROSOL AT BARROW, ALASKA DURING WINTER 1979-80 AS DEDUCED FROM ELEMENTAL TRACERS

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Abstract—A seven-element tracer system for regional pollution aerosol has been applied to 100 daily samples of aerosol from Barrow, Alaska during winter 1979-80, using regional signatures from eastern N America, Europe, and the Soviet Union. The results suggest that approximately 70% of most tracer elements came from the U.S.S.R., 25% came from Europe, and the rest came from N America. The large contribution from the U.S.S.R. is consistent with large-scale atmospheric flow patterns for that winter, in which air came strongly and persistently from central Asia northward to the Arctic. The small contribution from eastern N America agrees with previous circumstantial evidence. Apportionment of sulfate between Europe and the Soviet Union suggested that each contributed roughly 50%, however. The greater contribution of Europe to sulfate than to tracer elements is consistent with other data, including emission inventories for SO_2 and elements in the Soviet Union and Europe.

Key word index: Arctic, aerosol, long-range transport, tracers, factor analysis, discriminant analysis.

INTRODUCTION

Since the late 1970s, it has been recognized that the Arctic haze of winter is caused by large amounts of pollution aerosol being transported unusually efficiently from midlatitudes (Rahn and McCaffrey, 1980; Barrie *et al.*, 1981; Ottar, 1981; for example). Although certain features of the haze, such as its chemical composition and its seasonal variations, are now known quite well, major questions remain in other areas. One of the most difficult of these has been determining the location(s) of the major sources of Arctic haze aerosol. While it was relatively easy to identify the pollution component of the Barrow aerosol, it has proven much harder to localize its sources, even to the major continent(s) of origin.

The reasons for these problems are meteorological. In midlatitudes, the history of a polluted air mass can usually be reconstructed from synoptic configurations or from the trajectory of the air mass during the previous few days. In the Arctic, however, both these approaches are less reliable because the distances to sources are so great (5000–10000 km, or 5–20 days travel time) and the meteorological data are so sparse.

The first systematic trajectories to the Arctic were given by Miller (1981) as a 5-y climatology of 5-day back trajectories to Barrow, Alaska. The generality of Miller's four major conclusions illustrates the limitations of trajectory analysis for the Arctic: (a) the trajectories were longest from November to March and during August; (b) most of the long trajectories came to Barrow from the south; (c) over-the-pole flow to Barrow reached its maximum during March; and (d) direction and speed of the trajectories varied significantly from year to year and from season to season. Miller did not discuss the major continent(s) of origin of either the air or its pollution aerosol.

Clearly, an alternative to meteorological analysis is needed. Since 1980, we have been searching for regional elemental tracers which could be used to deduce the origin of pollution aerosol in the Arctic and other remote areas. The first successful regional tracer was the noncrustal Mn/V ratio, which is five-fold lower in eastern N America than in Europe (Rahn, 1981b). Rahn compared these regional ratios with noncrustal Mn/V ratios in the Arctic, and concluded that (1) Eurasia contributed more to Arctic aerosol than eastern N America did, and (2) aerosol of the N American Arctic appeared to be influenced by some source in addition to Europe (possibly the central Soviet Union) more than aerosol in the Norwegian Arctic did. Even though these conclusions agreed with the weight of meteorological evidence available at that time (Rahn, 1981a), they still had to be considered preliminary and supportive rather than definitive. Overall, the most important contribution of the noncrustal Mn/V ratio was to illustrate the feasibility of large-scale elemental tracers.

Since 1981, much more attention has been given to both the meteorology and the chemistry of Arctic haze. In the most extensive meteorological work, Raatz and Shaw (1984) studied the characteristics of 61 periods of elevated noncrustal Mn and noncrustal V at Barrow during 1976-80. They concluded that central Eurasian sources (probably mostly in the Soviet Union) dominated during winter, that western Eurasian (Europe and the United Kingdom) sources dominated during spring, and that N American and Far Eastern sources generally contributed little. Even this work was still

somewhat circumstantial, however, because it was based on only two chemical elements and their associations with large-scale, long-range flow patterns. Raatz and Shaw suggested that more-detailed chemical tracers would improve the resolution of source regions and remove some of the inconsistencies between the meteorological and chemical data.

We have recently developed an expanded and refined tracer technique which uses seven elements (As, Sb, Se, Zn, In, noncrustal Mn, noncrustal V) to resolve source areas of pollution aerosol more precisely and reliably than the noncrustal Mn/V ratio can (Rahn and Lowenthal, 1984, 1985; Rahn et al., 1985). With this system, it can be shown that distinct regional differences in pollution aerosol exist in both N America and Europe, that they do not change significantly during transport of 1000 km or more, and that aerosols of rural and remote areas take on only a small number of characteristic compositions which generally resemble those of midlatitude source areas. This article presents the first detailed application of this new tracer technique to Arctic aerosol.

SAMPLING AND ANALYSIS

A series of 100 daily aerosol samples was collected outside Barrow, Alaska at the Baseline Observatory of the NOAA Geophysical Monitoring for Climatic Change (GMCC) Program from 5 December 1979 through to 18 April 1980. The collection system, which consisted of a high-volume vacuum pump, a special wooden shelter, and 20 × 25-cm Whatman No. 41 cellulose filters, was similar to that used to collect weekly and semi-weekly filters described earlier (Rahn and McCaffrey, 1980). Air was drawn through the filters at the rate of $100 \, m^3 \, h^{-1}$.

All samples were analyzed by instrumental neutron activation for approximately 40 elements, including the seven used for tracing purposes. Samples were irradiated in the 2-MW research reactor of the Rhode Island Nuclear Science Center at a thermal neutron flux of $3 \times 10^{12} \, n \, cm^{-2} s^{-1}$ for periods of 5 min and 14 h. After decaying for 2 min to 3 weeks, gamma rays were counted on Ge(Li) detectors for 400 s to 3 h. Elemental masses were quantified by irradiating mixed standards containing the elements in question.

In addition, sulfate was measured by $BaSO_4$ turbidimetry, using a variant of the method of Tabatabai (1974) recommended by Wolfson (1980).

REGIONAL SIGNATURES FOR USE IN THE ARCTIC

For use in the Arctic, we prepared the five regional signatures shown in Table 1. All were scaled to Sb rather than to Se as in Rahn and Lowenthal (1984, 1985) because ratios to Sb appeared to be more stable than ratios to Se at Arctic sites. The reason for this is probably modest marine contributions to Se (Mosher and Duce, 1983), which become important at the lower end of Se concentrations observed at Barrow during winter.

The CEC signature represents pollution aerosol of the highly urbanized Central East Coast area of the United States, as described in detail by Rahn and Lowenthal (1985). The MW signature represents the American Midwest. It was derived by averaging the total midwestern contributions determined by chemical element balance (CEB) apportionments of seven samples taken at Underhill, Vermont during days in summer 1982 when episodic airflow brought large amounts of aerosol directly from the Midwest. The signature for the United Kingdom (UKS) is preliminary. It was derived from 11 samples taken at Rörvik, a coastal site in southern Sweden, during days of 1981–82 when cyclonic flow brought air directly from the U.K. This signature may also contain influences of western Europe. The European signature (EUR) was derived from five 2- and 3-day samples taken at Bear Island from 30 January to 13 February 1978, when air came to Bear Island from eastern and western Europe. The EUR signature is somewhat enriched in most elements (relative to Sb) compared to the UKS signature.

One source area currently emerging as very important to Arctic air pollution is the industrialized central Soviet Union, roughly the southern Urals–Kazakhstan vicinity. An estimate of the signature from this area (CUSSR) is given in the last column of Table 1. This version of CUSSR was derived from five 2- and 3-day samples taken at Bear Island from December 1977 through to February 1978, during periods when the aerosol was unusually enriched in As. This aerosol is

Table 1. Regional signatures of aerosol from Eurasia and eastern N America for use in the Arctic

	CEC (N = 12)	MW (N = 7)	UKS (N = 11)	EUR (N = 5)	CUSSR (N = 5)
As	0.74 ± 0.34	2.6 ± 0.4	1.74 ± 0.48	3.7 ± 0.6	10.0 ± 0.6
Sb	1.00 ± 0.30	1.00 ± 0.30	1.00 ± 0.29	1.00 ± 0.36	1.00 ± 0.28
Se	1.03 ± 0.45	4.4 ± 0.9	1.16 ± 0.34	2.2 ± 1.0	1.03 ± 0.48
Noncr. V	26 ± 10	1.54 ± 0.17	6.7 ± 2.0	11.2 ± 5.0	6.5 ± 2.0
Zn	28 ± 11	46 ± 4	44 ± 11	106 ± 44	45 ± 16
Noncr. Mn	3.4 ± 1.2	11.8 ± 1.7	7.8 ± 2.2	5.4 ± 2.8	4.4 ± 1.3
In (× 10³)	4.0 ± 2.9	7.9 ± 0.4	14.9 ± 8.5	—	—

very reproducible in composition, and appears at Bear Island (and other sites in the Norwegian Arctic) in pulses of a few days duration which are always associated with airflow from the central Soviet Union counterclockwise around one or more low-pressure areas centered between Spitsbergen and Novaya Zemlya. Because this circulation curves by 180° and brings polluted air from the south into Bear Island from the northeast, it has been named the 'return-flow' pathway. This same flow also brings pulses of SO_2 to Bear Island (Rahn et al., 1980). The surface synoptic map for one of these periods of high-As aerosol, 31 December 1977, is shown in Fig. 1. Back-trajectories to Bear Island for these situations, although limited in utility because of their distance, degree of curvature, and passage over the pack ice where wind and pressure data are sparse, generally point to the central Soviet Union and thus support our interpretation of the source of this unusual aerosol. As an example, isobaric trajectories for the same date, calculated by Joyce Harris of NOAA/GMCC in Boulder, Colorado, are shown in Fig. 2.

The accuracy of this signature is confirmed by abundant additional evidence. Pulses of similarly well-defined high-As aerosol are found throughout the Arctic, and are inevitably associated with airflow from the central Soviet Union. When enough samples are available for a site, these pulses appear as a distinct upper mode in frequency distributions of the As/Sb ratio. Figure 3 illustrates this for three sites in the Arctic, together with two in Europe for comparison. At Barrow and Bear Island during winter 1977–78, the As/Sb ratio had major modes centered on values of roughly 4 and 6. The third arctic site, the 'East Taymyr' area, refers to the location of a series of aircraft samples taken over the pack ice northeast of the Taymyr Peninsula (typically 79–85° N, 100–150° E, altitude 750–1500 m). Two modes are also seen here, but centered on slightly more divergent ratios of 2–3 and 6–8. As at Barrow and Bear Island, cyclonic flow directly from the central Soviet Union creates the upper mode of As/Sb. In the East Taymyr area, however, flow from the central Soviet Union is shorter and more direct, and hence the source can be assigned more confidently than at Barrow or Bear Island.

The shape of the upper mode at all three Arctic sites suggests that it may actually represent two unresolved modes centered on As/Sb ratios of roughly 6 and 10. Because the upper mode is created by airflow which is stronger, better defined, and from deeper in the Asian interior than that of the lower mode, we believe that the upper mode represents pure central Soviet Union
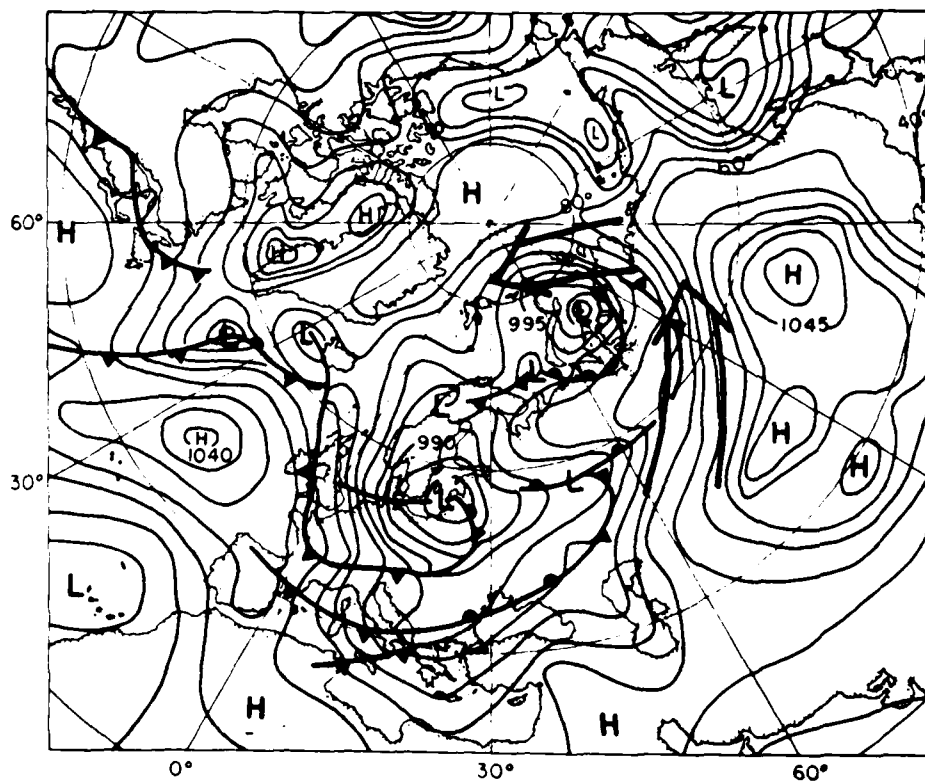

Fig. 1. Surface synoptic map for 0Z of 31 December 1977, during a period of high As/Sb at Bear Island. Pressures are given in mb, with isobars every 5 mb. Arrows indicate general direction of airflow near the surface.
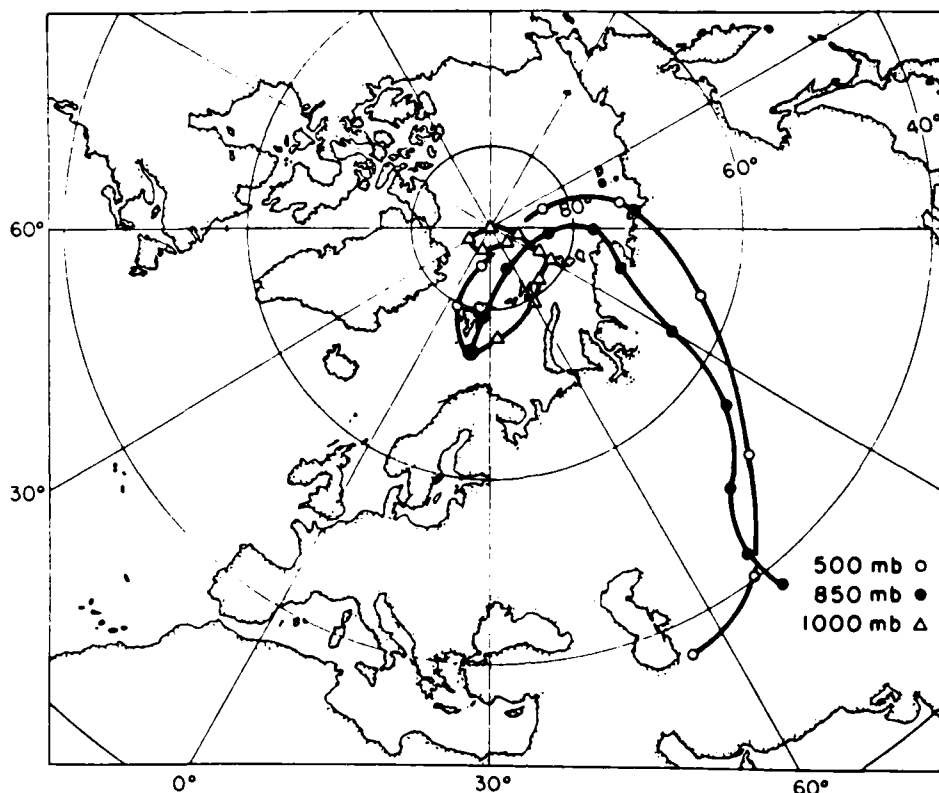
120

Fig. 2. Isobaric air-mass trajectories to Bear Island for 0Z of 31 December 1977. Marks shown each 24 h. Data from Joyce Harris, NOAA/GMCC, Boulder, Colorado.
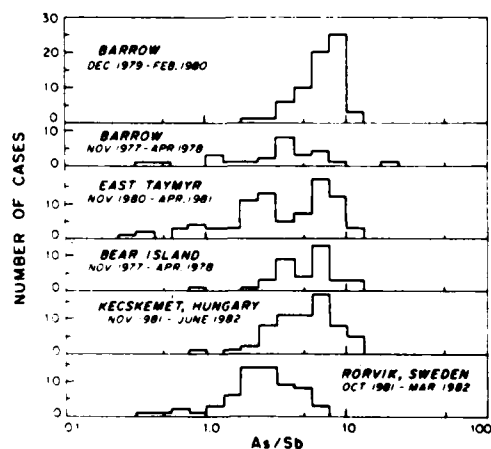

Fig. 3. Logarithmic frequency distributions of As/Sb in aerosol at three Arctic sites and two European sites.

aerosol and that the lower mode represents mixed U.S.S.R. sources and may occasionally contain a European component. Consequently, we have used the upper mode for our discussions and calculations.

Table 2 shows that the CUSSR signatures derived from upper-As/Sb modes in Bear Island, Barrow, and

the East Taymyr area are very similar to each other. We chose to use the one derived from Bear Island for subsequent statistical calculations because it resembled the mean signature closely and because the number of samples from Bear Island was closer to the number of samples in the other signatures, and thus would not weight the CUSSR signature unduly in discriminant analysis. For regional apportionment, however, the mean signature from all three sites could have been used equally well. Note that the Zn/Sb ratio in the CUSSR signature of Table 1 has been reduced by a factor of 69/46 (the ratio of values in the Bear Island CUSSR signature and in the Factor 1 discussed in the next section) to bring it into line with observations at Barrow during winter 1979–80 as well as nearer the source in the East Taymyr area. Adjustments like this are common in receptor modeling, and are an integral part of 'target-transformation' factor analysis (Weiner et al., 1970; Alpert and Hopke, 1980).

Elemental data directly from the central Soviet Union confirm the sense of our CUSSR signature. Rovinsky et al. (1982) report on a series of measurements of Pb, Hg, As and Cd from Hungary, Czechoslovakia, and five more-remote sampling sites within the western and central Soviet Union. Whereas the concentrations of Pb, Hg and Cd are five–ten times

121

Table 2. Elemental ratios in the upper As/Sb modes of aerosol at three Arctic locations

	As/Sb	Se/Sb	Noncr. V/Sb	Zn/Sb	Noncr. Mn/Sb	In/Sb ($\times 10^3$)
Bear Island, Dec. 1977–Feb. 1978 ($N = 5$)	10.0 ± 0.6	1.03 ± 0.48	6.5 ± 2.0	69 ± 22	4.4 ± 1.3	—
Barrow, Dec. 1977–Feb. 1978 ($N = 2$)	13.9 ± 8.1	2.2 ± 0.50	9.8 ± 1.9	86 ± 30	4.7 ± 1.6	—
East Taymyr area, Dec. 1980–Feb. 1983 ($N = 11$)	8.7 ± 0.9	0.83 ± 0.24	6.0 ± 3.4	47 ± 10	9.3 ± 3.2	34 ± 14
All sites ($N = 18$)	9.6 ± 2.7	1.03 ± 0.52	6.5 ± 3.1	58 ± 21	7.3 ± 3.5	—

lower at the U.S.S.R. sites than in Hungary and Czechoslovakia, the concentrations of As are the same or higher at the U.S.S.R. sites. Thus, As is enriched severalfold in U.S.S.R. aerosol relative to European aerosol, as shown independently by our CUSSR, EUR, and UKS signatures in Table 1. Interestingly, the highest concentrations of As in the U.S.S.R. were measured at Borovoje in northern Kazakhstan, their only site in the central Soviet Union. At more than 2 ng m^{-3} during summer, these concentrations are almost unprecedented for a remote area which is supposed to represent 'background' continental conditions. Conditions are even more extreme during winter: Rovinsky and Cherkhanov (1983) give 4 y of monthly-mean As concentrations at Borovoje, which show monthly maxima of nearly 10 ng m^{-3} As for 1–3 months every winter. By contrast, remote sites in eastern N America have maximum monthly-mean concentrations of As well under 0.5 ng m^{-3} (Rahn and Lowenthal, 1985).

One additional feature of Table 2 worth noting is the high In/Sb ratio of the CUSSR signature measured in the East Taymyr samples. In could not be measured in most samples from Barrow and Bear Island, because the higher concentrations of Na from sea salt at these surface sites raises the detection limit of In for neutron-activation analysis above the levels in most samples. The high In from the aircraft samples is useful because it confirms the implication from high As that nonferrous smelting contributes significantly to the CUSSR aerosol.

Could this central Soviet Union signature really be from the major nonferrous smelting complex at Noril'sk in the northern U.S.S.R. (69°N, 85°E)? While the CUSSR signature of Table 1 is similar to that of Noril'sk (Rahn et al., 1983), the airflow associated with the upper-mode East Taymyr samples, including those with the highest elemental concentrations, passed well east of Noril'sk. We interpret the similarity between the CUSSR and Noril'sk signatures to mean that CUSSR signature is also strongly influenced by nonferrous smelters, of which there are many in the central Soviet Union.

METHODS FOR DETERMINING MAJOR SOURCES OF BARROW AEROSOL

As described in the sections below, we have used factor analysis and discriminant analysis to give first indications of the major types of aerosol present in the 100 samples from winter 1979–80. The final contributions of the various source areas represented in Table 1 were then determined by least-squares CEB source apportionment, using the five signatures of Table 1 supplemented by a few others.

While attractive and objective in principle, both factor and discriminant analysis are sufficiently limited in practice that we could only use them as rough guides. Even though factor analysis has been used widely in receptor modeling, it performs best resolving sources of very different compositions, such as sea salt, crustal dust and pollution. Another difficulty with factor analysis is varimax rotation, which is one arbitrary choice among the infinite number which will reproduce the data, and hence is almost certainly not the most justified rotation. For the practical problem of resolving regional signatures from one another, as we try to do in these samples from Barrow, we have found that factor analysis can only isolate the dominant regional signature reliably (Rahn et al., 1985). Discriminant analysis is similarly limited in that it classifies samples into one or another source group rather than apportioning them among groups. However factor and discriminant analysis are useful for confirmatory purposes, and it is in this spirit that we use them.

FACTOR ANALYSIS

The concentrations of 12 elements in the samples were subjected to principal component analysis of the correlation matrix followed by varimax rotation, using a program in BMDP (1979). Although only the first three principal components had eigenvalues greater than one, both the three-factor and four-factor solutions were examined. The fourth factor was markedly weaker than the first three, because its variance after

rotation was 0.5, or only 4% of the total. Because its highest loading was a moderate 0.55 for sulfate, this factor did not reduce the dimensionality of the problem. The two solutions are shown in Table 3; the majority of the discussion to follow is based on the three-factor case. A similar three-factor solution was obtained using maximum-likelihood estimation (Morrison, 1976). Velicer (1977) has concluded that the common factor solutions, of which the maximum-likelihood type is one case, and the principal component solutions will be the same when the correct number of factors is retained for rotation.

Factor 1, which has loadings of 0.68–0.93 for As, Sb, Se, noncrustal V, Zn, nonmarine sulfate, and noncrustal Mn, clearly represents a general pollution component (marine sulfate was subtracted from total sulfate by using 0.25 for the sulfate/Na ratio in seawater). Factor 2, which has loadings of 0.98–0.99 for Al, Sc and Fe, represents a crustal component. Factor 3, with loadings of 0.97–0.98 for Na and Cl, represents a primary marine component, or 'sea salt'. As shown by the communalities, these three factors together accounted for 92% of the total variance.

Other factor analyses of Arctic aerosol have given similar results. For example, Heidam (1981) found that 70–85% of the variance of elements in Greenland aerosol was explained by the same factors of soil, sea salt, and pollution. Only occasionally did the pollution elements tend to split into more than one factor. In a more comprehensive analysis of data from the same stations, Heidam (1984) found evidence for at most five factors: soil, sea salt, and metallic, combustion, and automotive pollution factors. In general, however, the automotive factor was weak and the composition of the factors varied considerably from station to station.

The composition of Factor 1, the dominant pollution signature at Barrow, has been derived by multiplying the loadings of its elements by their standard deviations and scaling the results to unit Sb. This procedure follows in principle from the observation by Morrison (1976) that changes in scale of variables in factor analysis appear as equivalent changes in scale of their factor loadings, and follows directly from the derivation of Equation 20 by Henry et al. (1984). Because the elemental concentrations used in factor analysis are scaled by a factor of $1/s$ to get the correlation matrix (where s is the standard deviation of the element in the set of samples), the factor loading of an element may be scaled back to its relative concentration in that factor simply by multiplying by the element's standard deviation.

The composition of Factor 1 is shown in Table 4 together with the regional signatures of Table 1. Indium (In) was omitted from the factor analysis because it was not detected in enough of the 100 samples. Factor 1 is nearly identical to CUSSR and different from the other four signatures. Thus, factor analysis suggests that the central Soviet Union was an important, and perhaps even the dominant, source of pollution aerosol at Barrow during winter 1979–80.

Table 3. Factor analysis of the Barrow aerosol, winter 1979–80

	Varimax-rotated loading					Communality
	1	2	3	4		
As	0.90	0.13	0.22			0.87
Sb	0.89	0.11	0.34			0.97
Se	0.92	0.01	0.10			0.86
Noncr. V	0.93	0.08	-0.04			0.87
Zn	0.80	0.10	0.44			0.83
Nonmar. SO_4^{2-}	0.85	-0.03	-0.31			0.83
Noncr. Mn	0.70	0.64	0.12			0.92
Al	0.04	0.99	0.00			0.99
Sc	0.00	0.99	-0.01			0.99
Fe	0.14	0.98	0.04			0.99
Na	0.17	0.03	0.96			0.96
Cl	0.06	0.00	0.98			0.96
Variance	5.21	3.42	2.37		Average	0.92
As	0.94	0.11	0.14	-0.13		0.93
Sb	0.93	0.09	0.26	-0.12		0.96
Se 0.89	0.01	0.10	0.28		0.88	
Noncr. V	0.89	0.08	-0.04	0.27		0.88
Zn	0.83	0.08	0.38	-0.10		0.85
Nonmar. SO_4^{2-}	0.77	-0.01	-0.25	0.55		0.95
Noncr. Mn	0.72	0.63	0.07	-0.06		0.93
Al	0.05	0.99	0.01	0.00		0.99
Sc	0.00	0.99	0.00	0.01		0.99
Fe	0.15	0.98	0.04	0.00		0.99
Na	0.20	0.03	0.97	-0.02		0.98
Cl	0.10	0.00	0.98	-0.05		0.98
Variance	5.22	3.40	2.23	0.50	Average	0.94
	Pollution	Crust	Sea Salt	Pollution (SO_4^{2-})		

Table 4. Elemental composition of Factor 1 at Barrow compared to the regional
Eurasian and N American signatures of Table 1

	Factor 1	CUSSR	EUR	UKS	MW	CEC
As	9.2	10.0	3.7	1.74	2.6	0.74
Sb	1.0	1.0	1.0	1.0	1.0	1.0
Se	0.54	1.03	2.2	1.16	4.4	1.03
Noncr. V	4.4	6.5	11.2	6.7	1.54	26
Zn	45	45	106*	44	46	28
Noncr. Mn	5.2	4.4	5.4	7.8	11.8	3.4
In ($\times 10^3$)	—	—	—	14.9	7.9	4.0

DISCRIMINANT ANALYSIS

Linear discriminant analysis (Morrison, 1976) offers another preliminary impression of the major source areas for the Barrow aerosol of winter 1979–80. This technique first constructs 'source groups' from samples of known multivariate characteristics, then classifies samples of unknown origin into these groups according to their generalized squared distances from the groups. For the Barrow aerosol, the multivariate characteristics were the five X/Sb ratios discussed above, source groups were constructed for each signature of Table 1, and the unknown samples were the 100 from winter 1979–80. In essence, this procedure was a multivariate extension of our earlier approach using modes of the As/Sb frequency distributions. The samples used to construct the signatures of Table 1 were all classified correctly into their respective groups. 'Jackknifing', an option in the BMDP program which is used to test the robustness of a solution, gave the same results.

The Barrow samples were then classified into the five source groups, with the results shown in Table 5. Of the 100 samples, 17 were classified N American in origin, 20 were classified European, and 63 were classified Central Soviet Union in origin. Thus, discriminant analysis agreed with factor analysis that the Soviet Union was a major source of pollution aerosol at Barrow during winter 1979–80.

REGIONAL APPORTIONMENT OF SIGNATURE ELEMENTS AND SULFATE

A major limitation of discriminant analysis is that it cannot resolve mixtures of sources; a sample with contributions from more than one source will be classified into the group that it resembles most closely. To resolve mixed samples, such as are expected at Barrow, chemical element balance apportionment can

be used. This approach is essentially a weighted multiple regression with the elements in the samples and regional signatures as dependent and independent variables, respectively:

$$C_i = \sum_{j=1}^{p} A_{ij} S_j.$$

where C_i is the concentration of the ith element in an ambient sample, A_{ij} is the concentration of the ith species in the jth regional source, S_j is the derived strength of the jth regional source, or the 'regional coefficient' of the source, and p is the number of regional sources. EPA's CEB program (Williamson and DuBose, 1983) was used for the apportionments. Each element was weighted by its 'effective variance', which includes the variance of the element in both the sample and the signatures (Clutton-Brock, 1967; Hust and McCarty, 1967; Watson et al., 1984). Coefficients were constrained to positive or zero values; this procedure does not significantly bias the results (Rahn et al., 1985). Uncertainties were calculated with standard error-propagation procedures (Bevington, 1969).

Because of the near-hemispheric scale of this receptor study and the uncertainties concerning which source areas actually contributed to the Barrow aerosol, we felt that a single source apportionment should not be relied upon exclusively. Consequently, we have tried various combinations of source areas and sought consensus among the results. The various steps are described in the rest of this section.

We first apportioned the six signature elements plus sulfate in each of the 100 samples from Barrow into contributions from each of the five regional signatures of Table 1, with the summed results, or average apportionments for the winter, shown in Table 6. According to the last three columns of this table, the average concentrations of the signature elements were all accounted for to 25% or better. By the criterion

Table 5. Principal sources of aerosol samples of winter 1979–80 at Barrow, as derived from discriminant analysis

	CEC	MW	UKS	EUR	CUSSR	Total
Number of samples classified into source	0	17	16	4	63	100

Table 6. Average regional apportionments of elements in the Barrow aerosol of winter 1979–80, five sources

	CEC	MW	UKS	EUR	East N Am. (CEC+MW)	Europe (UKS+EUR)	CUSSR	Mean pred. (ng m⁻³)	Mean obs. (ng m⁻³)	Mean obs./pred.
					Apportionment, percent of mean predicted value					
As	0.1±0.2	1.6±0.7	4.0±1.0	0.9±1.3	1.8±0.7	4.9±1.7	93±3	0.85±0.02	0.86	0.99±0.09
Sb	1.4±1.6	5.0±2.1	18±5	1.2±2.0	6.4±2.7	20±6	74±6	0.108±0.008	0.124	1.19±0.27
Se	1.2±1.4	18±8	17±5	3.4±5.2	19±8	20±7	61±8	0.134±0.015	0.102	0.84±0.19
Noncr. V	5.6±6.4	1.2±0.5	18±5	3.3±4.9	6.8±6.4	21±7	72±8	0.72±0.07	0.55	0.79±0.19
Zn	0.9±1.0	4.9±2.1	17±5	4.4±6.6	5.8±2.3	21±8	73±8	5.0±0.4	4.8	0.95±0.18
Noncr. Mn	0.9±1.0	11±5	26±7	2.0±2.9	12±2	28±8	60±6	0.58±0.05	0.70	1.23±1.14
Nonmar. SO₄²⁻	11±4	25±9	23±6	1.4±3.1	36±11	25±7	39±5	1200±140	1180	1.04±0.47

proposed by Kowalczyk et al. (1978), that the observed/predicted ratio of a properly functioning receptor model should lie between 0.5 and 2, our five signatures thus constitute a properly predictive set for the Barrow winter aerosol.

A preliminary impression of the relative importances of the five regional sources comes from the magnitudes of their coefficients. Mean coefficients over the winter decreased in the following order: CUSSR (0.078), UKS (0.019), MW (0.0054), EUR (0.0021), and CEC (0.0015). Thus, the central Soviet Union signature dominated, UKS was a few times weaker, and the three other signatures were up to an order of magnitude weaker still.

The apportionments confirmed this impression. According to Table 6, five of the six signature elements came 60–74% from the central Soviet Union (CUSSR), 20–28% from Europe (UKS plus EUR), and 6–19% from eastern N America (CEC plus MW). Arsenic, which is unusually enriched in the central Soviet Union signature, came 93% from the Soviet Union, 5% from Europe, and only 2% from eastern N America. This result further reinforces those from factor analysis and discriminant analysis that the central Soviet Union was a very important source of Barrow aerosol during winter 1979–80. CEC and EUR seemed to be unimportant sources, as their uncertainties were all greater than 100%.

A typical meteorological mechanism for transporting aerosol from the central Soviet Union to Barrow is illustrated in Fig. 4, the surface synoptic map for 17 February 1980, which was during one of the most intense periods of Soviet Union aerosol at Barrow. Near the source, air flowed northward from the central U.S.S.R. between the low-pressure areas near Novaya Zemlya and the Asiatic high, which here appeared as a broad region of high pressure extending from the western U.S.S.R. into China. Over the pack ice, the air moved over the pole toward northwestern Canada in the strong pressure gradient between the Baffin Island low and the Chukchi high, which was really an extension of the Asiatic high. As the air approached Alaska, it curved westward under the influence of the Chukchi high. Although no parcel of air traversed this exact path, because pressure systems migrate during the several days required for the transport, the major ingredients of transport were all represented here. It is important to recognize that the intensity and location of the essential synoptic systems shown here may vary considerably from episode to episode, however. For example, the lows near Novaya Zemlya are often much larger and deeper than in Fig. 4, and may extend over much of the western U.S.S.R. In these cases, aerosol is drawn from farther south in the U.S.S.R. If the Chukchi high is weaker or centered farther south, the path across the pole may lead more directly to Barrow than in Fig. 4. Sometimes, when the Baffin Island low is located farther north, aerosol is deflected eastward after it reaches the pack ice near the Taymyr Peninsula, and follows the U.S.S.R. coastline to Barrow. These
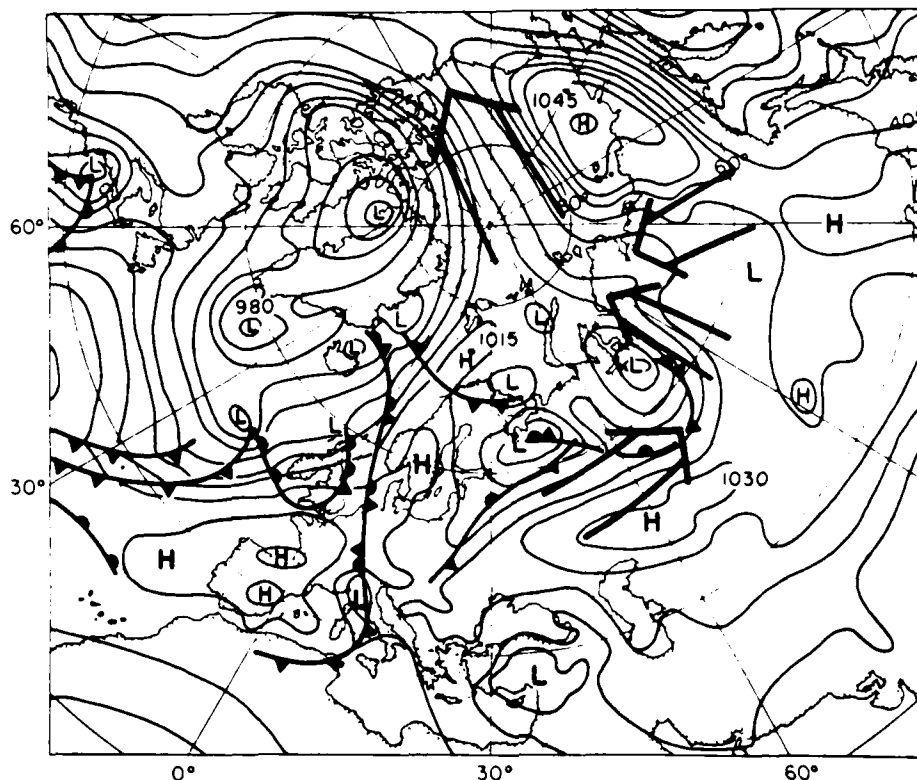
Fig. 4. Surface synoptic map for OZ of 17 February 1980, during a period of unusually concentrated aerosol with high As/Sb at Barrow, Alaska. Pressures are given in mb, with isobars every 5 mb. Arrows indicate general direction of airflow near the surface.

variations in pathway do not seem to produce any systematic differences in composition of the aerosol at Barrow, although the highest concentrations are associated with the most direct flow over the pack ice to Barrow.

Sulfate was apportioned among the five regional signatures by regressing its concentrations against the five regional coefficients for each sample derived from the signature elements, according to the procedure described by Rahn and Lowenthal (1984, 1985) and Rahn et al. (1985). As with the signature elements, effective-variance weighting was used, which took into account uncertainties of the regional coefficients, and all uncertainties were propagated and included in the final answer. The result was another regression coefficient for each signature, which represented the mean sulfate associated with that signature over the series of samples. This 'effective sulfate' was the sum of initial sulfate near the source plus that formed from SO_2 during transport. This indirect approach must be used for sulfate because a large fraction of its mass in remote areas such as the Arctic may be formed between source and receptor. By contrast, the proportions of most signature elements are stable during transport (Rahn et al., 1985), because they have no gas phase, are unreactive, and are removed at similar rates. Also, the

modest gas phase of Se described by Mosher and Duce (1983) does not appear to affect its proportions during transport. The contribution of a signature to sulfate in a sample is the product of the signature's effective sulfate and regional coefficient.

The apportionment of sulfate, as shown in Table 6, was weighted less to the U.S.S.R. (39 "₀) and more to Europe (25 "₀) and N America (36 "₀) than were the apportionments of signature elements. There are good reasons to believe that eastern N America actually contributed less to sulfate at Barrow than suggested by this calculation, however: (1) both CEC and MW signatures contributed little to the signature elements; (2) because the CEC signature was virtually never chosen for Barrow by the CEB apportionment program, and because all reasonable pathways from eastern N America to Barrow would result in mixtures of CEC and MW, many of the coefficients derived for MW may have been a result of colinearity; (3) the moderate colinearity between the MW and UKS signatures meant that some of the aerosol apportioned to MW may actually be from UKS; and (4) there was little or no evidence of direct airflow from eastern N America to Barrow during winter 1979-80 (Joyce Harris, NOAA GMCC, personal communication).

Accepting that eastern N America was not a major

126

source of sulfate for Barrow, we then sought to determine the relative contributions of Europe and the Soviet Union more precisely by reapportioning the Barrow aerosol between them alone. To represent Europe and the U.K., we used the UKS signature because the five-source apportionment nearly always chose UKS over EUR. We then apportioned the signature elements and sulfate at Barrow between the UKS and CUSSR signatures. The results are shown in Table 7. Except for sulfate and Se, whose contributions from the CUSSR signature increased by 16 % and 9 %, respectively, the percentages attributed to CUSSR were within 2 % of the values in Table 6. The final apportionment for sulfate was 55 % to the U.S.S.R. and 45 % to Europe. The quality of the sulfate apportionment, as measured by the obs./pred. ratio of 1.20, was as good as for the signature elements.

Thus, the two-source apportionment suggested that Europe was nearly as strong a source of sulfate for the Barrow aerosol as the Soviet Union was, while the latter was clearly the major source of the tracer elements. To test this important conclusion further, we

apportioned the Barrow aerosol in several other ways. First, we substituted the EUR signature for UKS and reapportioned with CUSSR in a fashion similar to Table 7. The result for sulfate was a 61 % to CUSSR and 39 % to EUR, as summarized under Case III in Table 8 (where for reference the sulfate apportionments of Tables 6 and 7 are shown as Cases I and II, respectively). The justification for using EUR in place of UKS was that the two signatures were very similar, and should easily substitute for one another. The mean sulfate was predicted nearly as well this way as it had been by the first two apportionments.

We then derived another European signature, called EURT, and used it in place of EUR to reapportion. The reason for generating the new signature was concern that EUR might not represent Europe well enough because it had been given such small coefficients in the original five-signature apportionment. EURT was constructed from the earlier western and eastern European signatures WEUR and EEUR (Rahn and Lowenthal, 1984) by combining five samples chosen randomly from each. The results of the

Table 7. Average regional apportionments of elements in the Barrow aerosol of winter 1979–80, two sources

	Percent of pred.		Mean pred.	Mean obs.	
	UKS	CUSSR	(ng m^{-3})	(ng m^{-3})	Mean obs./pred.
As	6.0 ± 0.5	94 ± 2	0.84 ± 0.02	0.85	1.06 ± 0.67
Sb	28 ± 1	72 ± 4	0.109 ± 0.004	0.123	1.20 ± 0.50
Se	30 ± 3	70 ± 6	0.116 ± 0.007	0.102	1.13 ± 0.70
Noncr. V	28 ± 3	72 ± 5	0.71 ± 0.03	0.54	0.77 ± 0.25
Zn	27 ± 2	73 ± 5	5.0 ± 0.2	4.8	0.94 ± 0.26
Noncr. Mn	40 ± 4	60 ± 4	0.58 ± 0.03	0.70	1.30 ± 1.28
Nonmar. SO$_4^{2-}$	45 ± 3	55 ± 2	1180 ± 40	1180	1.20 ± 0.71

Table 8. Regional apportionments of sulfate at Barrow during winter 1979–80 with different combinations of signatures

		Percent of predicted sulfate	Mean obs. (ng m^{-3})	Mean pred. (ng m^{-3})
I.	CUSSR	39 ± 5	1180	1200 ± 140
	UKS	23 ± 6		
	EUR	1.4 ± 3.1		
	MW	25 ± 9		
	CEC	11 ± 4		
II.	CUSSR	55 ± 2	1180	1180 ± 40
	UKS	45 ± 3		
III.	CUSSR	61 ± 2	1180	1240 ± 40
	EUR	39 ± 3		
IV.	CUSSR	46 ± 3	1180	1300 ± 60
	EURT (WEUR* + EEUR*)	54 ± 5		
V.	CUSSR	59 ± 18	1180	1240 ± 320
	UKS	35 ± 25		
	WEURS*	1 ± 4		
	EEURS*	6 ± 6		
VI.	CUSSR	44 ± 4	1180	1230 ± 80
	EURT	21 ± 4		
	MW	23 ± 4		
	CEC	11 ± 3		

*From Rahn and Lowenthal (1984).

sulfate apportionment with EURT and CUSSR are shown as Case IV in Table 8. They gave 46 % of the sulfate to the Soviet Union and 54 % to Europe.

To attempt to resolve the contributions from the various parts of Europe more finely, we repeated the apportionment with CUSSR, UKS, and the earlier western and eastern European signatures WEURS and EEURS (Rahn and Lowenthal, 1984). The apportionments of signature elements are shown in Table 9. Note how closely they resemble the earlier apportionments with European and N American signatures, by giving roughly 75 % of most elements (88 % of As) to CUSSR. This confirms both that eastern European aerosol can be distinguished from Soviet Union aerosol by our tracer system and that none of the aerosol attributed earlier to the U.S.S.R. is really from eastern Europe. The sulfate apportionments are shown as Case V in Table 8. They gave 59 ± 18 % to CUSSR, 35 ± 25 % to UKS, 6 ± 6 % to EEURS, and 1 ± 4 % to WEURS. Note how much larger the uncertainties are for this case than for the others. These high uncertainties were probably caused by the moderately high colinearity of the three European signatures, which increased the uncertainties of their regional coefficients. Table 10 shows the colinearity diagnostics for these signatures and CUSSR when applied to average Barrow aerosol from winter 1979–80, as derived from the test of Belsley *et al.* (1980). According to this test, the fourth 'component' has a 'condition index' of 62 and contains 86–99 % of the variance of the three European signatures. These three signatures are thus moderately-to-highly colinear. By contrast, CUSSR has no common variance on this term, and is thus not colinear with

these signatures. The colinearity of the European signatures is probably responsible for the unreliable results for sulfate.

The last apportionment combined the new European signature EURT with the N American signatures MW and CEC. The results are shown as Case VI in Table 8. It gave answers within a few percent of Case I. As with Case I, we feel that the large apportionment to MW (23 ± 4 %) was because of colinearity between MW and the European signatures.

Thus, all six apportionments agreed that the U.S.S.R. contributed smaller percentages of sulfate than of tracer elements to the Barrow aerosol of winter 1979–80. Considering everything, the answers were quite consistent, having a range of 39–61 % from the U.S.S.R. and a mean of 51 %, as opposed to 70–80 % of the signature elements from the U.S.S.R. We thus conclude that although the Soviet Union contributed 2–3 times the mass of signature elements to the Barrow aerosol than other sources (mostly Europe) did, Europe contributed as much sulfate.

Other data and reasoning support this conclusion. First, recall that in the four-factor solution shown in Table 3, the fourth factor drew off 20 % of the variance of sulfate from Factor 1, a much larger fraction than for any of the other elements. This meant that sulfate was not associated with the basic Central Soviet Union signature to the extent that the other pollution elements were. Possible reasons for this include secondary vs primary differences between sulfate and the other elements, and an additional major source area for sulfate. Both of these explanations are feasible: sulfate often appears on its own factor or with Se or

Table 9. Average regional apportionments of elements in the Barrow aerosol of winter 1979–80, four Eurasian sources

	Percent of mean predicted value				Mean pred. (ng m^{-3})	Mean obs. (ng m^{-3})
	UKS	WEURS*	EEURS*	CUSSR		
As	2.2	1.0	7.2	90	0.91	0.85
Sb	10.5	2.5	14	73	0.111	0.123
Se	12.4	2.1	8.2	77	0.109	0.102
Noncr. V	11.8	2.0	6.4	80	0.67	0.54
Zn	10.3	2.5	11.9	75	5.0	4.8
Noncr. Mn	15.3	3.8	21	60	0.60	0.70

*From Rahn and Lowenthal (1984).

Table 10. Colinearity diagnostics for four Eurasian signatures applied to average aerosol at Barrow, winter 1979–80

Number	Eigenvalue	Condition index	Variance-decomposition proportions			
			UKS	WEUR	EEUR	CUSSR
1	3.7	1.0	0.00	0.00	0.00	0.01
2	0.20	4.3	0.01	0.00	0.00	0.77
3	0.066	7.5	0.03	0.00	0.05	0.16
4	0.00096	62	0.96	1.00	0.95	0.06
			1.00	1.00	1.00	1.00

nitrate in a way that suggests secondary formation as a cause (Shaw and Paur, 1983; Stevens et al., 1984; for example); the proportions of Se and Zn on the fourth factor are high enough to be consistent with other measurements we have made of European aerosol. Second, we have seen a similar dichotomy between sulfate and trace elements in areas affected by strong nonferrous smelter signatures twice before: in spring 1982, the Noril'sk signature was detected at Barrow, but did not bring additional sulfate (Rahn et al., 1983); in New England, we detect aerosol from the nonferrous smelters of the Sudbury Basin which can account for 30–70% of the As and In of an entire season but less than 10% of the sulfate (Rahn and Lowenthal, 1985). Recall from above that high In and As imply that nonferrous smelting strongly influences the CUSSR signature. Third, estimates of emission of SO_2 and trace elements in Europe and the Soviet Union (Dovland and Saltbones, 1979; Pacyna, 1984a, b) suggest that Europe does indeed emit nearly twice as much SO_2 relative to most trace elements as the Soviet Union does, although the actual proportions vary considerably from element to element. But fourth, even if the ratios of SO_2 to elements were the same in European and Soviet Union emissions, the final ratios of sulfate to elements should be greater in transported European aerosol than in transported Soviet Union aerosol, because the warmer, more humid, and sunnier conditions in Europe favor conversion of SO_2 to sulfate more than in the more northerly Soviet Union.

ELEMENTS NEEDED TO RECOGNIZE THE CENTRAL SOVIET UNION SIGNATURE

In an earlier section, we noted that the most distinctive feature of the central Soviet Union signature was its high As. Here we wish to expand upon this point, because it illustrates one of the most important features of regional elemental tracers, namely that the ability to recognize a certain signature can depend critically on measuring a small number of key elements, occasionally even a single element. Rahn and Lowenthal (1984) noted an earlier case of this effect, where both they and Lannefors et al. (1983) had analyzed aerosol samples from southern Sweden but Lannefors et al. were unable to distinguish contributions from eastern and western Europe, presumably because their analytical technique, PIXE, did not measure As, In, or Sb. The central Soviet Union signature presents a similar problem. As shown in the following paragraphs, it is essential to measure As if CUSSR is to be distinguished with confidence from UKS, EUR, MW or CEC.

When a group of signatures is considered together, the relative 'tracer power' of the various elements or elemental ratios can be evaluated by stepwise discriminant analysis (BMDP, 1979). In this technique, variables are entered into the discriminant function one by one according to their ability to discriminate the

groups. The results of applying stepwise discriminant analysis to the As/Sb, Se/Sb, Zn/Sb, noncr. Mn/Sb, and noncr. V/Sb ratios in the CUSSR, UKS, EUR, MW, and CEC signatures are shown in Table 11. According to the first column, when all five signatures were considered, the As/Sb ratio was by far the most significant discriminator of the five ratios, as indicated by its 'F-value to enter' statistic. That none of the other ratios can replace As/Sb in its absence is illustrated by the second column, which shows that when the As/Sb ratio was removed from the calculation, the F-values and ranks of the other four ratios changed very little. The last column gives the F-values for the five ratios applied to the four signatures without CUSSR. While As/Sb still had the highest value, it had dropped by a factor of six relative to the five-signature case and came much closer to values for the other ratios. This means that the As/Sb ratio is a distinctive feature of the CUSSR signature, because As/Sb is much more useful in distinguishing CUSSR from the other four signatures than it is for the other four alone.

The importance of the As/Sb ratio to the CUSSR signature is shown in a different way in Fig. 5, where the

Table 11. Stepwise discriminant analysis of regional signatures from Eurasia and eastern N America

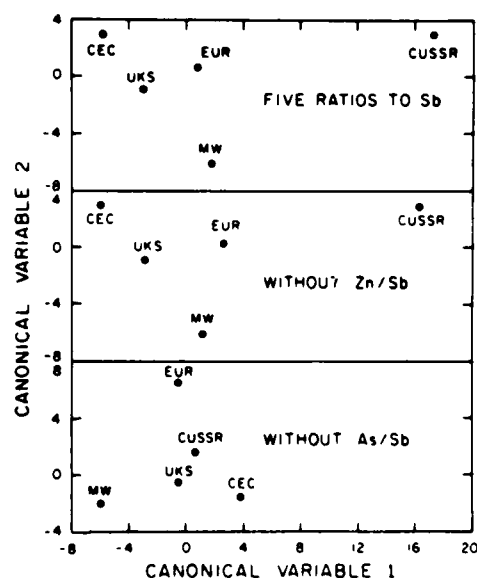|	F-value to enter		
	Five signatures		Without CUSSR
As/Sb	379	—	60
Se/Sb	41	38	20
Zn/Sb	35	31	13
Noncr. Mn/Sb	23	27	36
Noncr. V/Sb	14	17	12

Fig. 5. First and second canonical variables of the five signatures for various combinations of elemental ratios.

Table 12. Effect of removing Zn and As on regional apportionments of
Barrow aerosol, winter 1979-80

Signature	Mean coefficient ($N = 100$)		
	Six elements	Without Zn	Without As
CUSSR	0.078	0.078	0.050
UKS	0.019	0.022	0.045
EUR	0.0021	0.0022	0.0010
MW	0.0054	0.0048	0.0042
CEC	0.0015	—	—

first and second canonical variables for the five signatures are plotted for various combinations of elemental ratios. In the upper plot, for all five ratios, canonical variable 1 clearly separates CUSSR from the other signatures. In the middle plot, removing the Zn/Sb ratio hardly changes the results. In the lower plot, removing the As/Sb ratio brings CUSSR into the center of the cluster of the other ratios, i.e. eliminates CUSSR's distinctive character. Thus canonical variable 1 of the two upper plots was related strongly to As, which appeared to be critical in distinguishing the CUSSR signature.

Another confirmation of the need for As is given in Table 12. The first column shows the average regional coefficients derived from apportioning the 100 Barrow samples of winter 1979-80 with all six elements. As implied from the apportionment discussion above, the mean coefficient of the CUSSR signature (0.078) is much larger than the means of any of the other signatures (0.0015-0.019). When Zn is removed from the apportionment (second column), the coefficient of CUSSR stays the same and those of the other signatures change by only 5-15%. But when As is removed (third column), all coefficients change by much larger amounts: CUSSR decreases by 35%, UKS increases by 240%, EUR decreases by 50%, and MW decreases by 22%. In absolute terms, the loss of 0.038 in the CUSSR coefficient is nearly balanced by the gain of 0.026 in the UKS coefficient. Thus without As, CUSSR and UKS are seriously confused with one another.

Are there any other elements not measured here which might substitute for As in the CUSSR signature? In appears to be moderately similar in distribution among the signatures, but is often difficult to use because of its extremely low concentrations. Cd, which is generally enriched in effluent from nonferrous smelters, appears from the Central Soviet Union data of Rovinsky et al. (1982) not to be enriched enough there to substitute for As. The utility of elements such as Ge, Te, and Bi should also be investigated.

SUMMARY

In summary, then, during the winter of 1979-80, the Soviet Union appeared to be the major source of tracer elements in the Barrow aerosol, whereas Europe was an equivalent source of sulfate. It is too early to know whether these results are generally valid for the Arctic,

however, because the relative importances of European and Soviet sources vary from year to year. According to Fig. 3, for example, Soviet Union aerosol seemed less important at Barrow during winter 1977-78 than during winter 1979-80. Unfortunately, because of less-complete data for this earlier winter, sources of aerosol cannot be apportioned as reliably as for the second winter; climatologically valid apportionments must await new data from later winters. Nevertheless, the results from winter 1979-80 are sufficient to introduce a note of caution about assigning sources to the Arctic aerosol: the major sources of the tracer elements, which together amount to less than 1% of the mass of sulfate, may not necessarily be the major sources of sulfate or of the total Arctic pollution aerosol. For the winter of 1979-80, Europe and the Soviet Union would have to be considered equivalent sources of 'the' Arctic aerosol.

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The Acid Rain Whodunit

Clues to the culprits lead in several directions, depending on the weather

by Kenneth A. Rahn and Douglas H. Lowenthal

For several years our research group has been interested in determining the sources of the haze, or smog, that can often be seen over New England. Our interest comes from the knowledge that one of the most plentiful constituents of New England's haze is sulfate, a chemical combination of sulfur and oxygen that is associated with acid rain.

Haziness is the optical effect created by tiny particles of pollutants, collectively called aerosol, suspended in the atmosphere. Typical aerosol particles, with a 0.1-10 micrometer radius (1 micrometer equals 0.00004 inch), are so small that they can float in the atmosphere for several days. Carried by the wind, they may travel hundreds or thousands of miles from their points of origin before being washed out by rain or falling to the earth. Under very dry conditions—as in deserts, the Arctic during winter, or the upper atmosphere particles can be airborne for weeks or even months.

Because particles can move so far, determining the sources of regional haze is a knotty problem. At any moment, the aerosol at a given site can be a complex mixture of materials from a variety of distant and local sources. Separating the mixture into its component parts has challenged scientific minds for a decade.
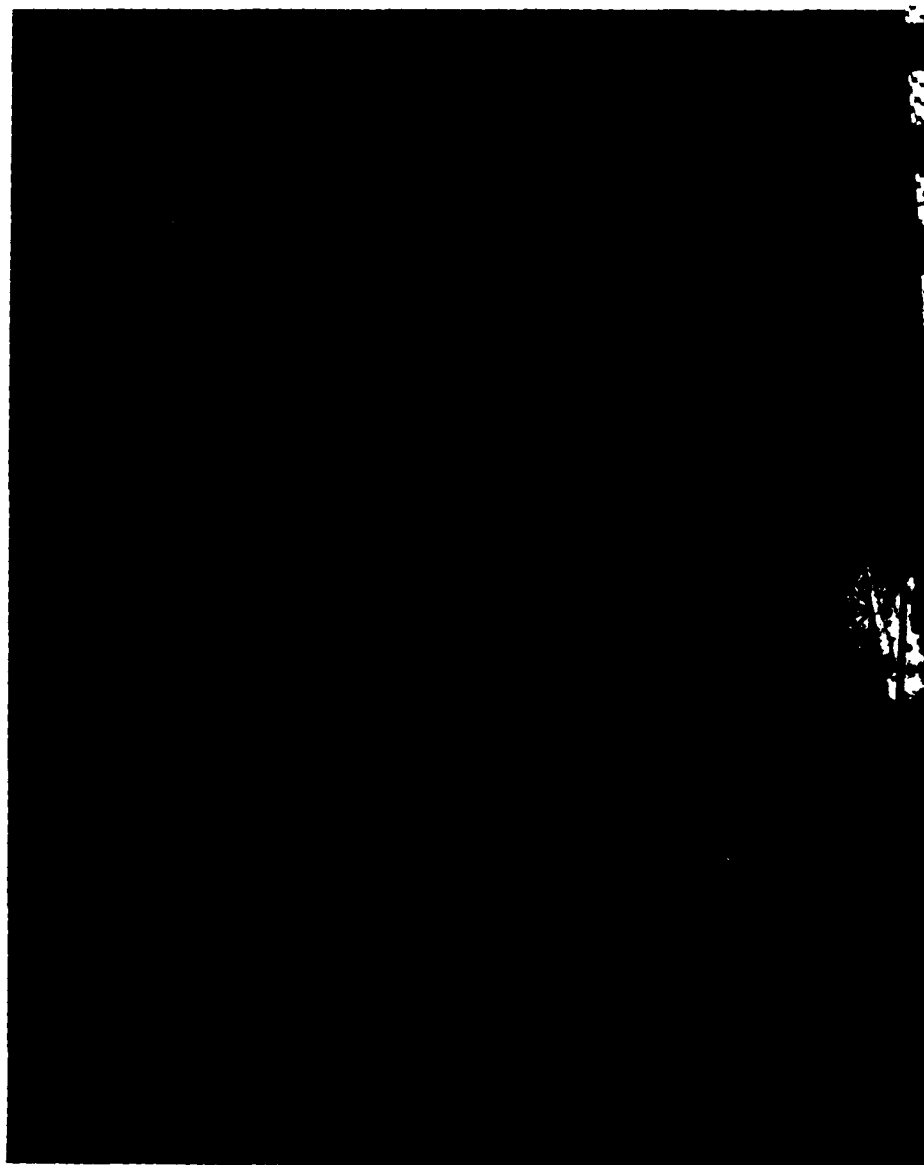
An obvious approach to pinpointing the origins of pollutants is to trace parcels of air backward in time by plotting past wind speeds and directions from weather maps and other recoverable information. But this method is severely limited because it cannot tell us which portions of the final mix come from which sources along the same pathway. Consider, for example, the common southwesterly winds of summer. Before reaching a site in New England, this air may have passed over the southeastern states, the mid-Atlantic states, and the heavily populated, almost continuously urban area that stretches up the east coast from Washington, D.C., to Boston. Air-mass trajectories alone say little about the relative influences of each of these areas on the final haze in New England. Chemical analysis of the smog, however, can be very helpful. As it happens, pollution aerosols emitted in the coastal

Northeast have a quite different chemical composition from those emitted in the interior of the United States. Analysis of these chemical differences allows us to distinguish local aerosols from distantly derived ones.

A major key to the chemical differences in regional aerosols is the type of fuel burned to generate electricity. Along the east coast, utility companies burn heavy residual oil, the product that is left

over after the lighter fractions of crude oil are removed to make gasoline, kerosene, and diesel and jet fuel. Relatively little residual oil is used inland, however, because it is so viscous that it must be kept heated if shipped from east coast refineries and ports. Therefore, most inland power plants burn coal.

Residual oil is rich in vanadium and nickel, and when burned, releases enough of those elements to give the local atmo-

developing since about 1980. Applying that system to New England, we have found that of the approximately twenty elements that are pollutants, seven--arsenic, antimony, selenium, zinc, indium, manganese, and vanadium—are particularly useful for tracing purposes. In time, other elements are sure to be added to the system; we have already begun to investigate nine other potential tracer elements.

The tracer system was originally developed to enable us to understand the sources and transport of pollution aerosol in the Arctic. That application has been very successful and was described two years ago in *Natural History* ("Who's Polluting the Arctic?" May 1984). To determine the major chemical "signatures" of regional pollution in eastern North America, we sampled aerosol in the Northeast and Midwest. From numerous samples taken at various locations, among them Narragansett, Rhode Island; Underhill, Vermont; Allegheny Mountain, Pennsylvania; and Akron, Ohio, we were able to identify the local components and found that there are at least five different regional signatures: two along the east coast, two in the Midwest, and one from the nonferrous smelters in southern Ontario and Quebec. Statistical analysis shows that for all practical purposes these signatures differ from one another.

The mathematics of fitting the five signatures to a sample is quite involved, and the results are hard to verify. But there is abundant circumstantial evidence that our apportionments of chemicals are meaningful. We analyze a season of daily aerosol samples from a site, calculate the proportions of regional pollutants in each sample, display those quantities in the form of a graph, and then look for associations between the aerosol patterns and weather patterns. We have found that in most cases the chemical and meteorological evidence corroborate each other in terms of where the pollution is coming from on any given day.

We concluded that some locally derived aerosol is always present, to which distantly generated aerosol is occasionally added. About half the time the aerosol is predominantly local and half the time a

sphere a distinctive stamp. Coal, in contrast, is relatively free of vanadium and nickel but rich in such elements as selenium and arsenic. (None of these characteristic features exist in isolation, however; each is distinctive only in comparison with other elements.)

Other differences between east coast and interior pollutants are related to population density. The aerosol in heavily populated regions has its own characteristic combination of elements, including zinc and antimony from the incineration of refuse and lead from automobile exhaust. These elements are higher in urban aerosols than in rural and remote aerosols and can serve as additional markers that differentiate coastal and interior aerosol pollution.

We deal with all these regional differences simultaneously in a system for tracing regional elements that we have been

133

sizable amount has come from distant midwestern sources. That makes good common sense because Narragansett is surrounded by northeastern sources of pollution and can therefore never escape their influence. Midwestern sources, though, can be cut off entirely by nothing more than winds coming from a different direction. Even the durations of the midwestern surges, or pulses, of aerosols—commonly between two and four days—make sense: high- and low-pressure areas, which control the patterns of large-scale airflow to Narragansett, also fluctuate in periods of a few days to one week.

Through a cooperative program with Rich Poirot of the Vermont Agency of Environmental Conservation, we have received samples from Underhill, Vermont, for the same periods as those from Narragansett. We found that most major pulses of midwestern aerosol appear and disappear within a day or two of the same time at Narragansett and Underhill and that the arrival of pulses from the Canadian smelters are just as closely coordinated. From this near-simultaneity we infer both that region-wide measurements are valid and that chemical changes in the northeastern atmosphere are synchronized with regional, rather than local, events. In general, when the polluting aerosol at Narragansett (or Underhill) is primarily of local origin, the air is either locally stagnant or moving into New England from the north. When a distinctly midwestern aerosol is superimposed on the local pollution, there is large-scale airflow from the Midwest.

We took daily local samples at given sites and averaged them over three-month periods, and we have been reassured to find that our average apportionments of pollution aerosol in New England vary little from site to site and from season to season.

Our findings at Narragansett and Underhill were as follows. Most—60 to 80 percent by weight—of the zinc and manganese in Narrangansett air was attributable to local northeastern sources, with the remainder coming from the Midwest. (These elements are present in about equal concentrations in distant and local aerosols, so that one might expect nearby sources to supply the greater share.) Also consistent with expectation, the northeastern sources accounted for more than 90 percent of the oil-combustion elements, such as vanadium, which are relatively uncommon in midwestern emissions. Canada supplied our study sites with about 50 percent of their arsenic and 30 percent of their indium both elements particularly rich in emissions from Canadian smelters. Interestingly, half or more of the sulfur

Pollutant Pathways

H

15 July
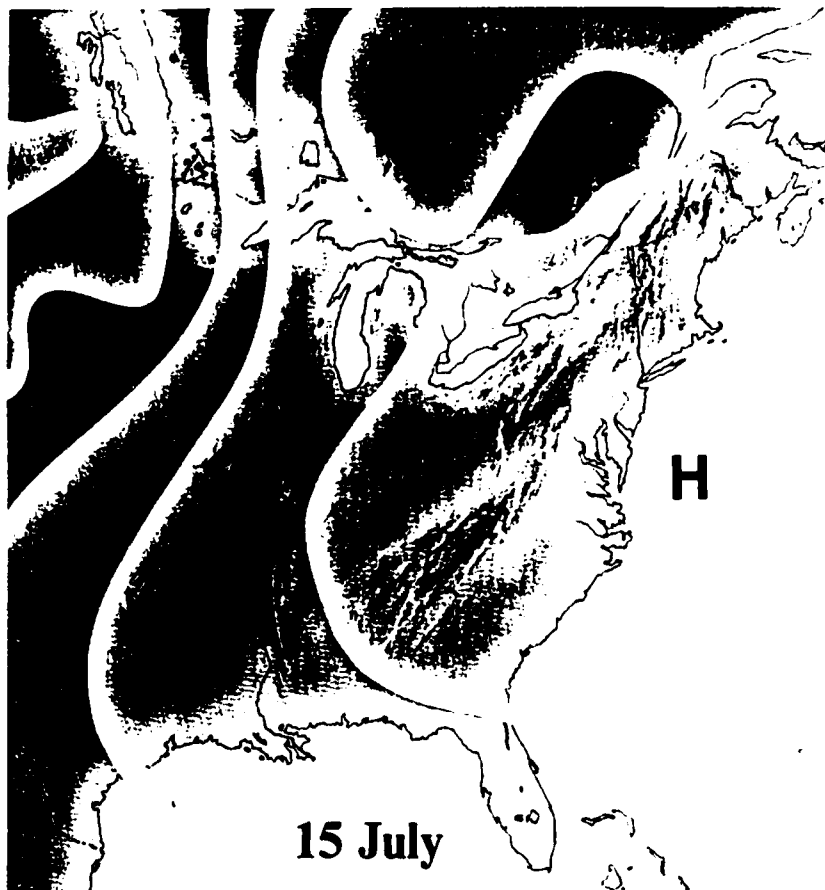
Relative Amounts of Pollutants
Narragansett, Rhode Island

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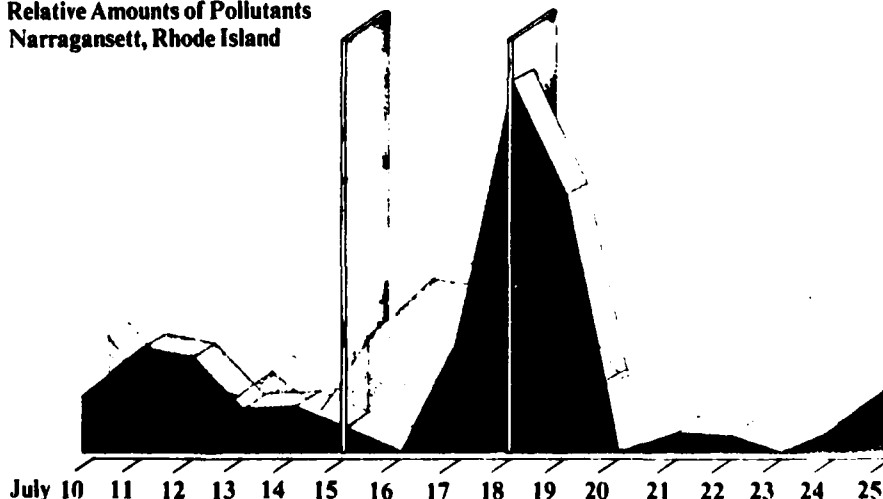
Are pollutants in the air over Narragansett, Rhode Island, mainly local in origin or mixed with particles from the Midwest? It depends upon the weather. On July 15, 1982, an air mass stagnated over much of the Northeast, blocking the flow of air (maroon arrow) from the Midwest. On that day, locally generated pollutants far outweighed distant contributions. Three days later, a low-pressure system advanced eastward across southern Canada, deforming a high-pressure system over the South Atlantic. A stream of air flowed between the systems, bringing a strong influx of midwestern pollutants to Narragansett.

18 July

H

Northeast
Contribution

Midwest
Contribution

Midwestern pollutants come to the Northeast in surges. Between July 10 and July 30, 1982, locally generated pollution was fairly constant in Narragansett, while midwestern aerosols arrived in one major pulse, peaking on July 18. Two days later, after a cold front had passed through the area, midwestern pollutants were virtually absent from Narragansett air.

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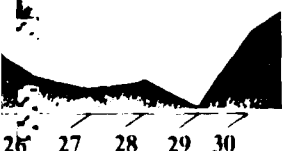
and selenium measured at the Narragansett study site was traceable to the midwestern sources. This is as high a contribution from the Midwest as we find for any element.

Of these apportionments, sulfate is of greatest current importance because it is the largest contributor to acid rain. Since the Midwest emits ten times as much sulfur dioxide, the parent of sulfate, as the Northeast does, the roughly 50/50 split we found between local and distant sources of sulfate means that the amount of distant midwestern aerosols has been reduced in the northeastern atmosphere by a factor of ten. We think that this level of reduction, large as it might seem at first glance, is plausible. Recall that about half the time, there is no midwestern aerosol in Narragansett. The distance between the nearby sources and those 600 to 800 miles away in the Midwest could easily account for another factor of five or so. Computer models for the long-range transport of sulfur, which include, among other variables, detailed meteorological information, also tend to yield a reduction of roughly ten for those distant sources.

We believe that our technique for determining the geographical derivations of chemical pollutants is significant because before we applied it to acid rain precursors in New England, the general assumption was that the pollutants had been generated solely in the Midwest. With the new knowledge that some local sources are *always* present, a good start can be made in controlling the original pollution.

In spite of the amount of work that has gone into developing and applying our regional elemental tracer technique, and the successes it has produced, we know that it is only a beginning. More chemical elements and regional signatures are needed, as well as studies at a greater number of receptors in the Northeast. The Southeast, where emissions of sulfur dioxide have been increasing faster than in the rest of the country, should also be studied, along with Mississippi River Valley emissions. Most importantly, the tracer technique needs to be extended to rain and snow themselves so that sources of acid rain can be studied directly. Since it rains only about 5 percent of the time in the northeastern United States, layering of the atmosphere and the selective trajectories of rainstorms could easily lead to sources of acid rain that differ considerably from sources of surface aerosol. Encouraged by the success we have had so far with our chemical tracer system, we see no reason why the same system cannot be applied to the contaminants in rain with equal success.

ENVIRONMENT

Acid Rain's 'Fingerprints'

Tracing the culprits

To date, a numbing 3,000 scientific papers and seven major government reports have weighed in on the causes and effects of acid rain, leaving little doubt about the basic alchemy that turns the emissions of electric plants and vehicles into the hard rain that damages lakes and soils. But opponents of mandatory emission controls seize on several unanswered questions to justify their opposition—one of the most divisive: where does the rain come from? Suspicions have long centered on the Midwest, where burning of high-sulfur coal creates millions of tons of the sulfur dioxide from which acid deposition forms. But some studies have shown that local sources might produce fully *half* the acid rain falling in the Northeast, suggesting that those states would do well to look to their own backyards before badgering the Midwest to clean up its act. Now, however, researchers at the University of Rhode Island have uncovered persuasive evidence that most of the Northeast's acid rain does indeed originate far away.

To trace acid rain, URI's Kenneth Rahn and Douglas Lowenthal identified chemical "fingerprints" in air masses. It happens that certain activities, such as smelting,

'Return address': *Factory pollution*

and certain fuels, such as heavy oil, are concentrated in specific geographic areas. Since manufacturing and combustion spew characteristic pollutants into the air, this pattern is tailor-made for tracing air masses: the pollutants in them act like return addresses, indicating the air's origins. For instance, the Midwest burns more coal than the East, which burns more heavy oil. Coal combustion produces the elements selenium and arsenic; heavy oils generate vanadium. Identifying a high ratio of selenium in an air mass blowing over the Narragansett shore, then, tells scientists that it likely began its journey in the Midwest.

Air mass: When the URI team applied the tracer system to air masses reaching Vermont and Rhode Island, they estimated that roughly 50 percent of the aerosol sulfates originated in the Midwest, and 50 percent came from local sources. But aerosols are, at best, a measure of the *precursors* of acid rain, not of acid rain itself. Extending the tracer system to actual precipitation yielded dramatic results. Rahn and atmospheric chemist Roy Heaton now find that roughly 80 percent of the sulfates in rain and snow falling on the Northeast probably come from the Midwest.

How can 80 percent of the acid rain originate in the Midwest while only 50 percent of its precursors bear that return address? The answer lies in meteorology. Rain forms high in the atmosphere; taking samples of rain, then, is tantamount to sampling high-altitude air. Because it requires time for air to rise after it has mixed with pollutants near the ground, the higher a sample of contaminated air, the longer it has been aloft. And the longer air has been aloft, the farther away it originated. Until now, scien-

tists had only suspected, but had not demonstrated, that the altitude of air pollutants is tied to their regional origin. Says Rahn: "These results underscore the importance of emissions in the Midwest to acid rain."

The tracer technique has been criticized in the past, but this spring the Environmental Protection Agency accepted it in principle as a valid way to find the origin of pollutants. And this week Rahn and Lowenthal are being awarded a patent on the process. Still, the URI results will likely matter less to the lawmakers considering controls on acid rain than economics and politics do. Congress is now contemplating two bills addressing acid rain. The House version, with 169 cosponsors from both parties and all regions of the country, would reduce emissions of sulfur dioxide by 9 million tons a year by 1997; the Senate bill, with 21 cosponsors, would cut emissions by 12 million tons—about 50 percent—and would also control pollutants like ozone and carbon monoxide. Hearings on the Senate bill are set to start after Labor Day, and the bills' supporters already think they have enough science on their side; opponents, including the Reagan administration, call for still more study, seeking definitive answers to how acid deposition affects forests and how much cuts in sulfur emissions would cut acid rain. The URI results may not tip the balance toward controls, but they do add evidence to the case against the modern scourge.

SHARON BEGLEY *with* MARY HAGER *in Washington*

Trout Redoubt

Almost nothing epitomized the transformation of fecund lakes into cesspools so much as the blight of Lake Ontario. By 1960 trout that had once seemed as dense as goldfish in a dentist's office had been driven to extinction by overfishing, predation and pollutants ranging from PCB's to sewage. But after a decade of efforts to control both predators and run-off, a joint Canadian-American program began restocking Ontario with trout yearlings. Now the efforts have paid off: trout have reached sexual maturity and are spawning in significant numbers for the first time in 30 years.

Researchers caught 75 fry this spring, and scientists regard that as an encouraging sign that Lake Ontario again offers a hospitable environment for sport fish. More significantly, it provides hope that polluted waters can be yanked back from the brink of ecological doom. But it's too soon for anglers to celebrate: officials request that to help the recovery effort, fishermen throw back any trout they hook.

Riding the Winds

New data on tracking pollutants in air suggest that up to 80 percent of sulfates in the Northeast's acid rain come from the Midwest.
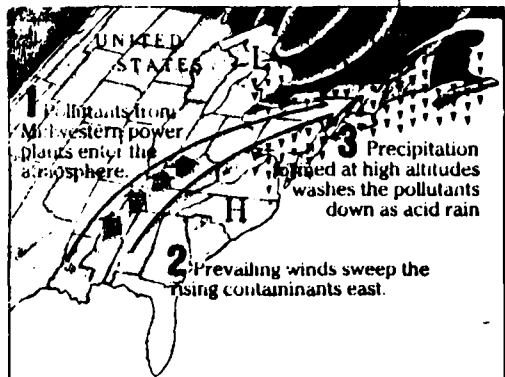

1 Pollutants from Midwestern power plants enter the atmosphere.

2 Prevailing winds sweep the rising contaminants east.

3 Precipitation formed at high altitudes washes the pollutants down as acid rain.

THOMSSON - NEWSWEEK

United States Patent [19]

Rahn et al.

[11] **Patent Number:** **4,603,575**

[45] **Date of Patent:** **Aug. 5, 1986**

[54] **ELEMENTAL TRACER SYSTEM FOR DETERMINING THE SOURCE AREAS OF POLLUTION AEROSOL**

[75] Inventors: Kenneth A. Rahn; Douglas H. Lowenthal, both of Narragansett, R I

[73] Assignee: Board of Governors for Higher Education, State of Rhode Island and Providence Plantations, Providence, R.I

[21] Appl. No.: 686,655

[22] Filed: Dec. 27, 1984

[51] Int. Cl.⁴ G01N 15/06
[52] U.S. Cl. 73/28; 436/56
[58] Field of Search .... 73/23, 28, 170 R, 432 PS; 436/56, 25, 26, 27, 28

[56] **References Cited**

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4.325.122 4/1982 Parks et al .... 73/170 R
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Primary Examiner—Stephen A. Kreitman
Attorney, Agent, or Firm—Thompson, Birch, Gauthier & Samuels

[57] **ABSTRACT**

A method of determining source areas of pollution aerosol. Selected pollution derived, fine particle tracer elements from within the source region are measured. The measured results are expressed as ratios to one of the tracer elements. A signature of the source region is determined from modes in the logarithmic frequency of the ratios of the tracer elements. Measurements are made of the tracer elements from a receptor region and elemental ratios constructed. The elemental ratios from the receptor region are compared with the signatures from possible source regions to determine the most probable source region.
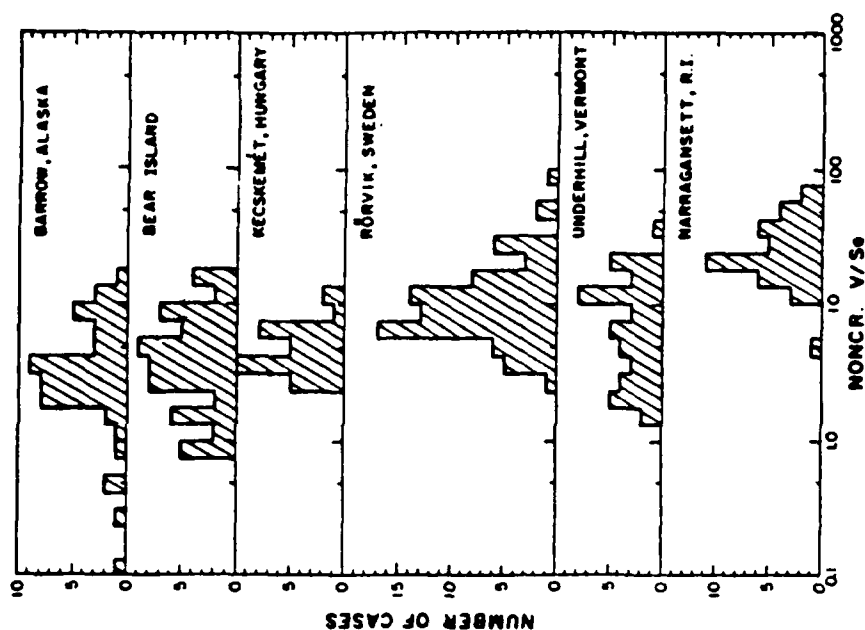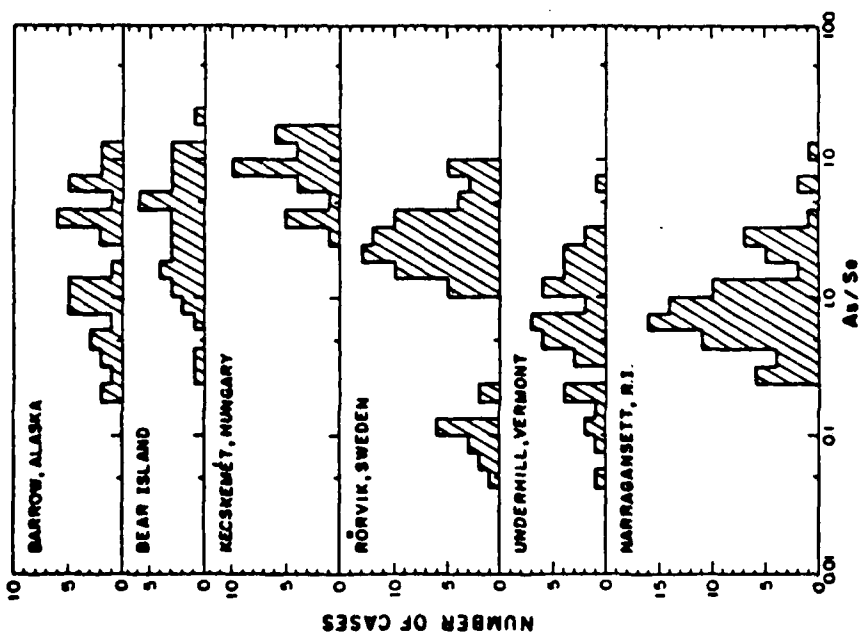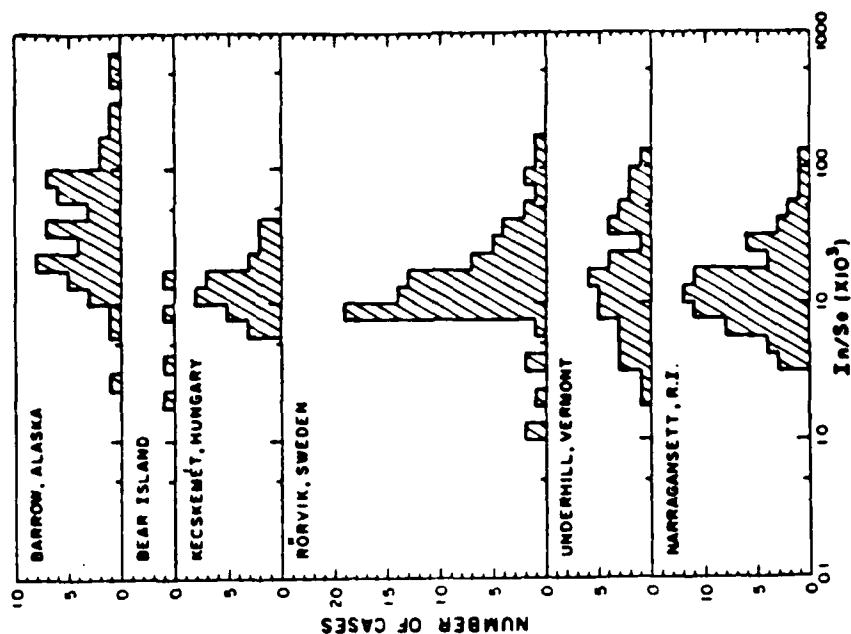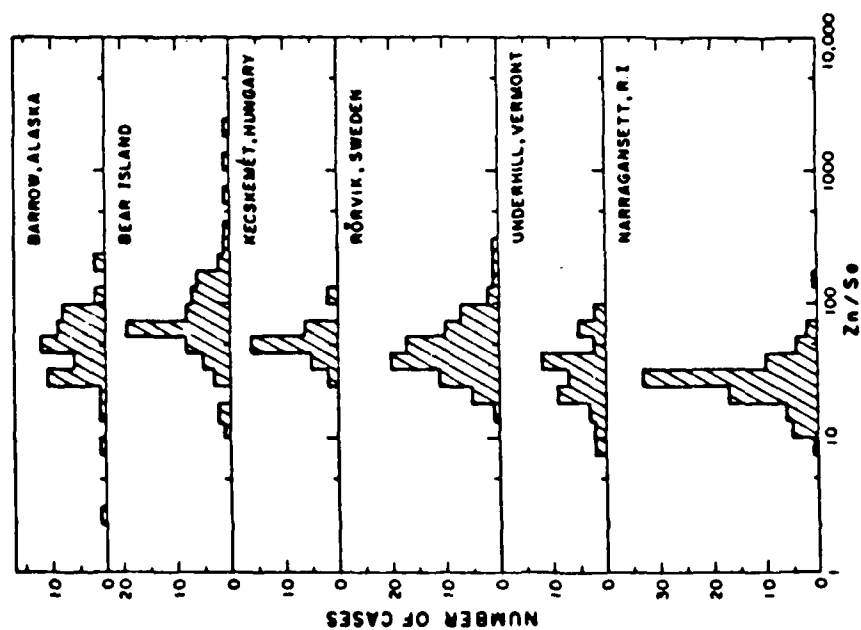
9 Claims, 7 Drawing Figures

FIG. 1B

FIG. 1A
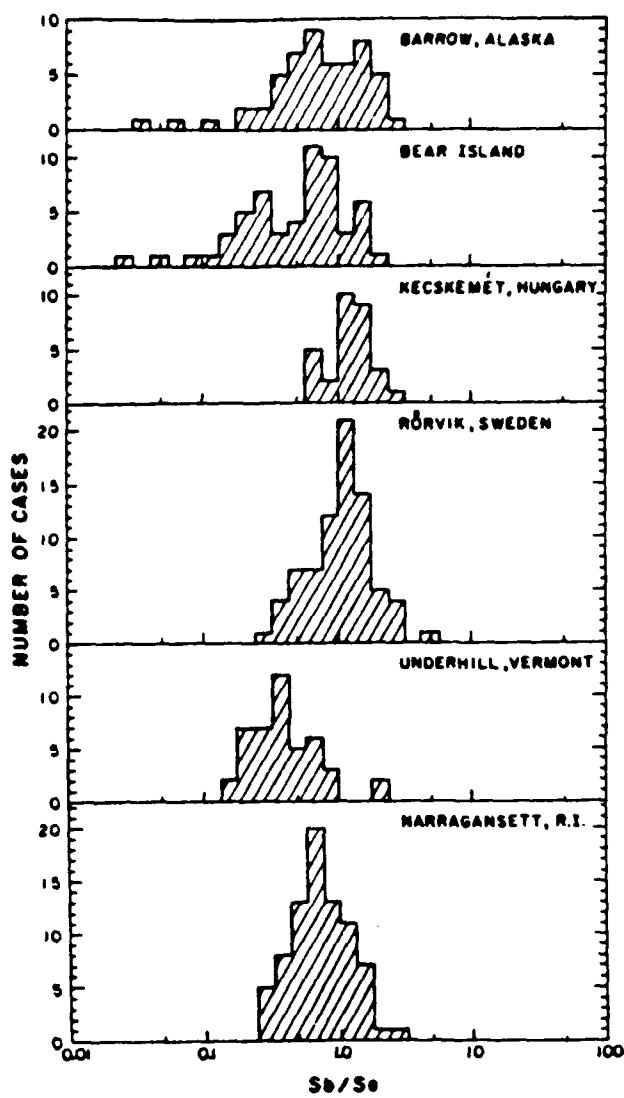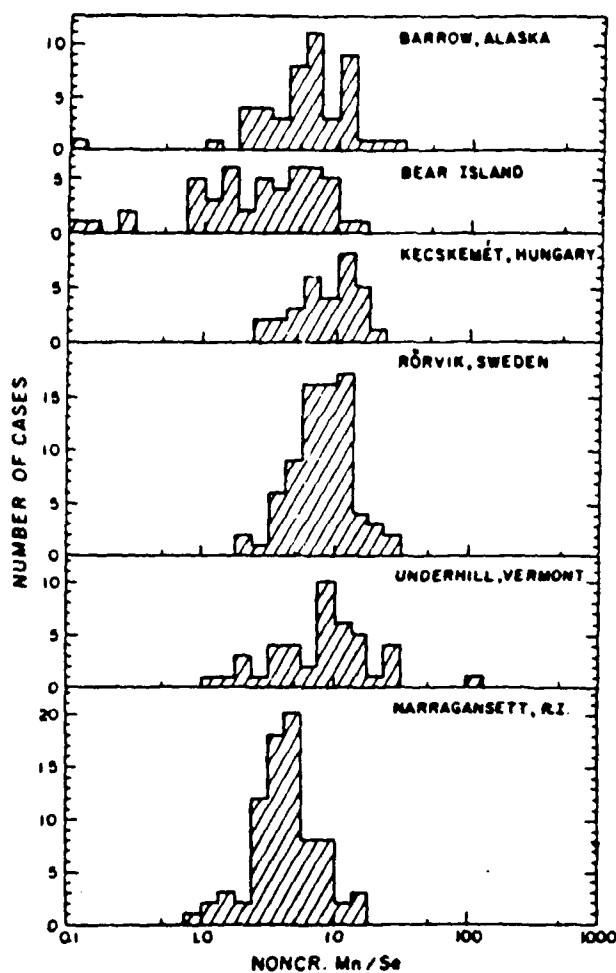
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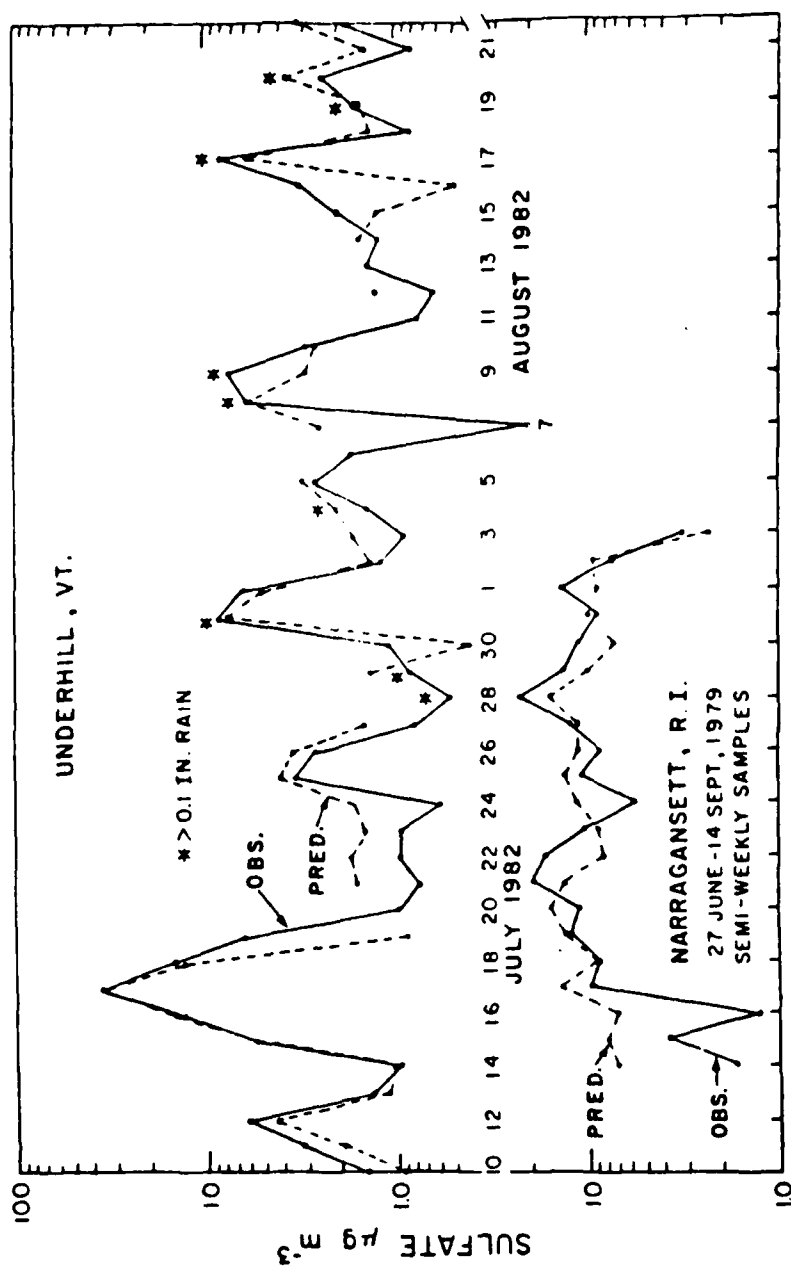FIG. IF

FIG. IC

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FIG. ID

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FIG. IE

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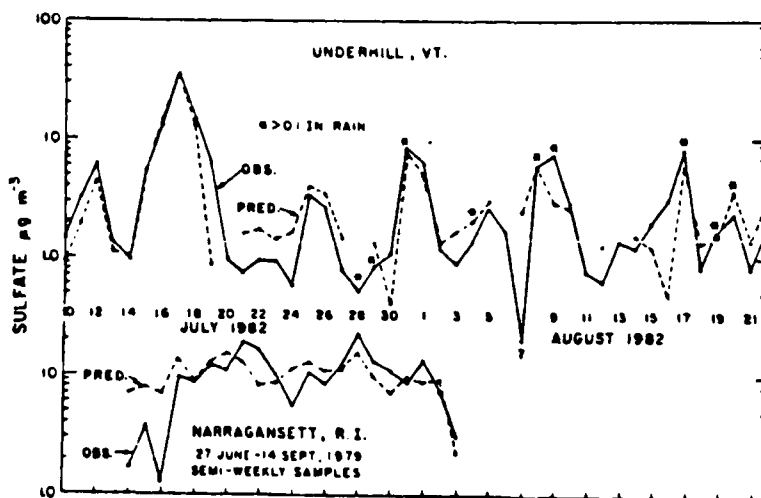
FIG. 2

ELEMENTAL TRACER SYSTEM FOR DETERMINING THE SOURCE AREAS OF POLLUTION AEROSOL

BACKGROUND AND BRIEF SUMMARY OF THE INVENTION

The routine transport of pollution aerosol through long distances is increasingly recognized as an important aspect of atmospheric science. Atmospheric transport on the scale of 1000 to 10,000 km is now invoked regularly to explain the results of aerosol studies in rural and remote areas. P. J. Samsonb, *J. Appl. Meteorol* 19, 1382 (1980); K. A. Rahn and R. J. McCaffrey, *Ann. N.Y. Acad. Sci.* 338, 486 (1980); R. D. Borys and K. A. Rahn, *Atoms. Environ.* 15, 1491 (1981); L. A. Barrie, R. M. Hoff, S. M. Daggupaty, ibid., p. 1407; C. Brosset, *Ambio* 5, 157 (1976).

But long-range transport has created a new set of interpretive problems. While it is relatively easy to identify pulses of transported pollution aerosols in remote areas which are otherwise clean, it is often difficult or impossible to pinpoint the source areas of these aerosols. (At distances of a few hundred kilometers or more, source areas are normally much more important than point sources).

Sheer distance can cause problems. For example, it has been extremely difficult to decide whether the important sources of pollution aerosol observed at Barrow, Alaska, are located in North America, Europe, or Asia. With air-mass trajectories from these sources being 5000 to 10,000 km or more in length and representing travel times of 5 to 10 days or more, pure meterological techniques have not led to consensus about even the continents of origin, much less particular regions within the continents. J. M. Miller, *Atoms. Environ.* 15, 1401 (1981); E. R. Reiter, ibid., p. 1465; D. E. Patterson and R. B. Husar, ibid., p. 1479.

The configuration of sources can also make identification difficult. In the northeastern United States, for example, where the source areas of acid aerosol and precipitation are currently in dispute, distances of transport are much shorter (1000 km or less) but the spatial pattern of sources is complex. As a result, trajectories to areas of concern such as the Adirondacks or New England often pass over several strong source areas in their last few hundred kilometers. No available transport model can reliably apportion the contributions of these sources to the final sulfate, acid, or other ubiquitous constituents of the pollution aerosol.

There is thus a need for a more direct way to identify distant sources of pollution aerosol. Such a capability would be of practical as well as scientific importance, because it could be extended ultimately to determining source areas of acid precipitation. It may cost as much as $20 billion to $100 billion to reduce emissions of sulfur dioxide in the eastern United States over the next decade, controlling the wrong sources would be a very costly error.

The present invention embodies a method to detect regional sources of pollution on a regional scale. The efforts to date in this field can only trace individual emitters over smaller distances

Pollution aerosol contains all elements, no true tracers, or elements unique to specific source areas, exist. But it is reasonable to expect the proportions of at least some elements to vary with source area because different areas have different mixes of the major aerosol

sources (combustion, industry, transportation, and so on), different mixes of fuels, fuels from different origins, different industrial bases, and different degrees of pollution control. However, the number of regional elemental signatures, the magnitude of their differences, and the elements involved cannot be predicted; they must be determined empirically.

In general, regional tracers as used in our invention are constructed and used quite differently from urban tracers. Elemental signatures used to deduce sources of urban aerosol by receptor-oriented techniques (G. E. Gordon, *Environ. Sci. Technol.* 14, 792 (1980).) are usually derived from either point sources or specific types of sources (automotive exhaust, for example). Regional aerosols, by contrast, are mixes of many sources and should thus resemble one another much more than signatures within an urban region should. Similarities among pollution aerosols have been recognized for years (K. A. Rahn, "*The chemical composition of the atmospheric aerosol,*" Technical Report, Graduate School of Oceanography, University of Rhode Island (1976).), and many have doubted whether useful regional differences could be found. We have determined that characteristic regional signatures do exist, many of which are very different from one another.

The two keys to deriving regional signatures are finding the right elements and handling the data with the appropriate statistical techniques. The "marker-element" approach sometimes used in urban studies (where the contribution of a source is evaluated by a single element) cannot be used with regional signatures because of their great similarities. The opposite approach, constructing signatures from all available elements, is practiced in some urban studies but addes too much noise to regional pollution signatures. The best approach seems to be a compromise-limit regional signatures to those few elements with the greatest tracer power.

Several requirements should be met by elements and signatures before they can be used in a regional tracer system: the elements should be pollution-derived, sampled and measured accurately, emitted stably and homogeneously in each region, and present on particles small enough to be transported long distances; each signature should remain recognizable during transport. Our preliminary assessment indicates that all these requirements are met adequately; we illustrate several of them in the description that follows. Nevertheless, some of these requirements, such as conservation of proportions during transport, are sufficiently critical that we have built routine checks into our operating system.

In our invention a system in which the relative abundances of selected elements in pollution aerosol (suspended particles) are used to determine the region(s) from which it has originated. The technique can be applied at distances of hundreds to thousands of kilometers from the sources, i.e., in regions ranging from rural to very remote, and where conventional approaches such as emission inventories, air-mass trajectories, and long-range transport models fail. For example, both Canada and the United States now agree that the several long-range transport models currently in use for predicting the origins of sulfate and acidity are unverified and unverifiable in the near future. We thus view our elemental technique as a powerful alternative.

Our invention distinguishes from the known prior art in that we recognize and document the existence of

3

regional elemental signatures. The technique described hereinafter represents our formalized method for developing these signatures and using them quantitatively.

The techniques has several key features. It preferably uses seven pollution-derived, fine-particle elements in the signatures (arsenic, selenium, antimony, zinc, indium, manganese, vanadium). These elements are chosen from the 40 or so that we can measure by neutronactivation analysis because they are the most pollution-derived and are determined best, i.e., have the lowest analytical uncertainties. This list of elements is not static, it can be altered as needed, and should expand in the future as other analytical techniques are employed. For elements such as manganese and vanadium, a substantial fraction of whose mass comes from suspended soil dust, only the pollution-derived component is used. It is important that only fine-particle elements be used in this tracer system, so that they will remain in the atmosphere for long periods and their proportions will not change during transport.

Regional signatures are preferrably built from the six elemental ratios to selenium rather than the seven absolute concentrations. Ratios are used to correct for changes in elemental concentration due to dispersion and removal during transport.

The regional signatures are built up from multiple samples at multiple sites within each region. Because any region can be influenced by aerosol from outside it, only some of the samples from a given region can be used to characterize it. They must be chosen from the total set of samples with care. We generally use some combination of a priori knowledge of the region, modal analysis of the frequency distributions of the elemental ratios, and meterological analysis to do this. To be safe, the signature of a region should not be considered known until samples inside and outside the region agree. From the final set of samples representing a region, geometric means and geometric standard deviations are calculated from each elemental ratio to selenium. The collection of six means and six standard deviations is the elemental signature of that region.

A sample of aerosol from a receptor region can be assigned to a most-likely source area by discriminant analysis, which compares the six elemental ratios to those of samples from possible source regions in a multivariate sense and assigns probabilities that the sample came from each region.

Contributions of several source regions to the signature elements can be determined by least-square apportionment, using various calculational routines and elemental weighting factors.

Contributions of several source regions to sulfate aerosol (formed mostly from SO₂ during transport) or other nonsignature constituents can be determined by regressing the regional coefficients of a suite of samples against their sulfate concentrations.

Unique features of our tracer technique are its set of seven elements and its regional approach. Elemental tracers have been used to determine the sources of urban aerosol for several years. Our regional approach, however, uses different elements, a different form for the signatures, builds up the signatures according to a different protocol, and manipulates them with different statistical techniques.

We have determined that well-defined regional signatures exist in both North America and Europe. In North America, we have measured both midwestern and coastal influences on pollution aerosol at Underhill, Vt.,

4

Narragansett, R. I., High Point, N. J., and Allegheny Mountain, Pa. The meterology of many of the samples in question was sufficiently obscure that it could not have revealed their origins with any confidence. In Vermont, the majority of the sulfate aerosol in summer comes from the Midwest; in Rhode Island, it comes from the Northeast. We have also detected a signature from the nonferrous smelters of the Sudbury Basin and shown that their contributions to sulfate aerosol in New England during summer are small. The role of these smelters has been discussed for years. we have provided the first direct answers. In Europe, we have shown that the aerosol of a particularly strong pollution episode in Sweden and Finland came from East Europe, not West Europe or the United Kingdom. In the Arctic, we have shown that aerosol at both Barrow, Alaska and Bear Island (Norwegian Arctic) is dominated by Eurasian rather than North American sources. At each site, aerosols from different parts of Eurasia have been detected.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1a, 1b, 1c, 1d, 1e and 1f show the frequency distributions of six elemental ratios at six sites in eastern North America, Europe, ad the Arctic; and

FIG. 2 shows the observed and predicted sulfate for 21 semiweekly samples during June tp September 1979.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The first regional tracer was the noncrustal Mn/V ratio Atoms, Environ. 15, 1457 (1981). (The noncrustal component of an element is used here to mean the mass present in excess of that calculated from a crustal reference element like Al, Si, Fe or Ti, assumed to be totally crustal in the aerosol (a), and a crustal reference material such as bulk rock or soil (r). The formula typically used to calculate the noncrustal component of element X is

$$\text{Noncrustal } X_a = \text{total } X_a - Al_a (X/Al)_r$$

In most cases, global mean crustal rock or soil is satisfactory; occasionally, local rock or soil must be used as reference material). This tracer was designed to determine whether Arctic aerosol originated mainly from Europe or eastern North America. The noncrustal Mn/V ratio demonstrated the general feasibility of regional elemental tracers and stimulated the development of more sophisticated tracing systems. At present, we are using a seven-element tracer system involving As, Sb, Se, Zn, In, noncrustal Mn, and noncrustal V. The design of this system and several of its applications are discussed below.

These seven elements were chosen from the 40 to 45 that we have measured by neutron activation as best meeting the criteria of being pollution-derived, fine-particle (The dividing line between fine and coarse aerosol is usually taken to be radius ~1 μm. This corresponds to the approximate breakpoint between (i) particules which penetrate to the lung and those which do not, (ii) coarser particles formed by mechanical subdivision (of soil and seawater, for example) and finer particles formed by coagulation or nucleation, and (iii) the original German "large" and "giant" ranges of particles), and accurately analyzable (Instrumental neutron activation normally allows As, Sb, Se, Zn, and noncrustal V to be determined in replicate aerosol samples to uncertainties of 5 to 15 percent, and In and noncrustal Mn to

5

0 to 40 percent. Differences between elements in simultaneous samples are usually less than 10 percent; for ratios, most of this difference disappears). Potential tracers rejected because of larger analytical uncertainties included Cu, Ni, Ga, Mo, Ag, Cd, Sn, W, Au, and Ig. With better analysis, any or all of these might be included in the system. Lead and elemental carbon are strong candidates which should also be investigated. Indium, whose analysis is poorer than those of the other six elements, was retained because of its great utility in tracing nonferrous smelters, K. A. Rahn, N. F. Lewis, D. H. Lowenthal, in *Receptor Models Applied to Contemporary Pollution Problems*, SP-48, Air Pollution Control Association, Pittsburgh, PA, 1982 p. 163.

Our regional signatures consist of six elemental ratios to Se. Ratios are used to normalize for variable meteorogical effects such as dispersion and removal. Se is used in the denominator because it is a general pollutant found at similar concentrations in diverse source areas and hence will not bias the ratios toward any particular region. In spite of Se's ubiquitous but modest vapor phase of 15 to 30 percent near the surface (B. W. Mosher and R. A. Duce, *J. Geophys. Res.* 88, 6761 1983)) and its natural sources such as volcanoes, it works well as a normalizing element in regions as remote as the Arctic in winter. We tested Zn as an alternative denominator (because of its similarly low coefficient of variation) and obtained the same results as with Se. Other general pollution elements such as Pb or C might also be considered for the denominator.

The signature of a source region cannot be derived in a completely straightforward fashion because most regions can be affected by pollution aerosols transported from other regions. To eliminate such interference, we have developed a protocol which involves multiple samples at multiple sites inside and outside the region. At each site, at least 100 (ideally) daily samplers are taken and analyzed for the tracer elements. Logarithmic frequency distributions of the various X/Se ratios are then constructed and examined for the presence of modes, or maxima, which represent characteristic aerosols for the sites. The meterological characteristics such as of atmospheric stagnation can be combined with chemical characteristics of the samples in a mode to give a good idea of its source. By combining the modal information from several sites in a region, its aerosol may usually be distinguished from those transported from neighboring regions. Local aerosol may also be identified from periods of atmospheric stagnation. As a final check, regional signatures are verified by sampling downwind of the region. This also shows whether any elemental ratios change significantly during transport.

To date, we have used filter samples of total aerosol for our tracer system. In effect, this provides size-segregated data because the tracer elements chosen are mostly submicrometer. True fine-particle samples would probably improve the tracer system by reducing the variability of elemental ratios and allowing mixed-mode elements such as Fe, Co, and Cr to be considered. But how much the improvement would be is not yet known, and size-segregated samples are much smaller and not readily available from many regions of interest. When elemental tracer techniques are eventually applied to precipitation, total aerosol will be a more appropriate reference than fine-particle aerosol, for coarse particles are scavenged more efficiently by precipitation than are fine particles.

6

Factor analysis, while useful for understanding broad elemental relations and the general sources of pollution aerosol of a site, has not been particularly successful in selecting elements as tracers or defining regional signatures. The reason for this seems to be that any technique which is based solely on single measures of similarity between elements (such as correlations) in a collection of samples does not adequately reveal the complex relations implicit in mixed frequency distributions.

FIG. 1 shows the six X/Se distribution for six sites at which we have reasonable amounts of data: Narragansett, R. I., and Underhill, Vt., in eastern North America; Kecskemet, Hungary, and Rorvik, Sweden, in Europe; and Barrow, Alaska, and Bear Island, Norway, in the Arctic (Seventy-nine Narragansett samples taken semiweekly during February–April and June–August 1978 and January–March and June–September 1979, 43 Underhill samples taken daily during July–August 1982; 76 Rorvik samples taken for 1 to 3 days each during fall and winter 1981–1982; 31 Kecskemet samples taken daily during fall and winter 1981–1982; 66 Bear Island samples taken for 2 to 3 days each during winter 1977–1978, 54 Barrow samples taken simiweekly from October 1977 to May 1978) Depending on element and location, one or more modes are seen in each distribution. The modes are reasonably symmetric (that is, log-normal), with geometric standard deviations of 1.4 to 1.6 (68 percent of the points found within a total factor of 2 to 3). Some modes have geometric standard deviations as low as 1.2. The presence of these modes shows that a few major types of pollution aerosol are found at each site.

More types of pollution aerosol may be present at a site than are revealed directly by the major modes, however. Broader-than-normal modes may be composed of two or more unresolved modes, as seems often to be the case for Zn/Se and Sb/Se, for example. Small features may represent infrequent appearances of aerosols which are more important elsewhere. An example of this is the small upper mode of As/Se at Rorvik (ratios of 8 to 10), which coincides with the principal mode (6 to 12) at Kecskemet (we show below the upper mode at Rorvik was created by a pulse of aerosol from eastern Europe). Another example is the low shoulder of Zn/Se at Narragansett (ratios of 10 to 20), which has been resolved into a discrete mode by subsequent shorter period samples. The real number of modes in most distributions is not known and may be considerably larger than the number apparent from FIG. 1.

Membership in most modes is organized; that is, samples in a certain mode of one distribution are usually found together in other distributions. For example, the samples from eastern Europe which comprise the upper As/Se mode of Rorvik also comprise the low shoulder of noncrustal V/Se (ratios of 3 to 6). This illustrates that well-defined pollution aerosols with recognizable signatures do exist. As shown below, they can usually be identified with specific geographic source areas.

At present, we use the modes of FIG. 1 only qualitatively. To derive signatures of pollution aerosol for specific regions, we use subsets of the modes composed of samples deemed most representative. With experience, it should be possible to increase the numbers of samples used to define signatures.

Twelve regional signatures, six from North America and six from Europe, are shown in Table 1. The signature of regional New England (NE) was derived from

145

7

four daily samples at Underhill Aug. (4 to 7 1982), in aged Canada air masses which had not been affected by the large nonferrous smelters of the Sudbury Basin. The outstanding feature of this signature is its low As/Se ratio, which we interpret as indicating minimal coal influence. We have also detected this signature in Narragansett and South Portland, Me. (the small low-As mode at Narragansett in FIG. 1 is associated with this kind of aerosol.

8

gional, there). The Washington, D.C. (WASH). signature came from grand averages of individual average concentrations from ten sites in the Washington area during August and September 1976 (G S Kowalczyk, G E Gordon, S W Rheingrover, Environ.Sci Technol 16, 79 (1982). As in New York. Zn was reduced by 30 percent in an attempt to represent aerosol from the central mid-Atlantic states. The interior (INT) signature was derived from four daily samples in Underhill,

TABLE 1

Geometric mean elemental signatures for source aerosols in North America and Europe (geometric standard deviations in parentheses)

Source	N	As/Se	Sb/Se	Noncrustal V/Se	Zn/Se	Noncrustal Mn/Se	In/Se (× 1000)
Individual sources							
SCANS	5	2.8 (1.3)	0.94 (2.0)	24 (1.3)	43 (1.5)	5.2 (1.8)	9.5 (1.7)
WEURS	5	1.88 (1.2)	1.01 (1.4)	5.8 (1.3)	37 (1.1)	6.5 (1.2)	13.1 (1.6)
WEURH	5	3.5 (1.1)	0.75 (1.3)	7.2 (1.8)	56 (1.4)	6.8 (1.7)	11.1 (2.2)
EEURF	5	7.2 (1.2)	1.33 (1.3)	7.8 (1.2)	54 (1.1)	10.0 (1.2)	13.1 (1.3)
EEURS	3	7.3 (1.1)	1.73 (1.1)	4.8 (1.2)	66 (1.1)	13.7 (1.2)	15.1 (1.2)
EEURH	4	8.9 (1.0)	1.18 (1.1)	5.2 (1.3)	48 (1.1)	8.9 (1.8)	9.8 (1.4)
NE	4	0.13 (1.4)	0.45 (1.3)	11.3 (1.2)	32 (1.2)	9.2 (1.3)	9.8 (1.9)
BOS	3	0.68 (1.5)	0.82 (1.8)	35 (1.2)	37 (1.1)	4.1 (1.2)	5.3 (1.1)
NYC	3	1.10 (1.1)	1.63 (1.7)	11.1 (1.3)	40 (1.1)	6.5 (1.3)	9.6 (1.6)
WASH	4	1.46 (1.2)	0.82 (1.2)	9.9 (1.2)	22 (1.2)	4.0 (1.8)	7.1 (1.2)
INT	4	0.92 (1.2)	0.28 (1.4)	1.96 (1.4)	10.8 (1.3)	2.6 (1.5)	3.9 (1.7)
SONT	3	8.0 (1.2)	0.75 (1.2)	1.77 (1.9)	57 (1.1)	13.9 (1.1)	46 (1.7)
Regional means							
SCANS	5	2.8 (1.3)	0.94 (2.0)	24 (1.3)	43 (1.5)	5.2 (1.8)	9.5 (1.7)
WEUR	10	2.6 (1.4)	0.87 (1.4)	6.4 (1.6)	45 (1.4)	6.6 (1.5)	12.1 (1.9)
EEUR	12	7.8 (1.2)	1.37 (1.2)	6.0 (1.4)	54 (1.1)	10.4 (1.5)	12.3 (1.3)
ECOAST	14	0.58 (2.9)	0.80 (1.8)	13.8 (1.7)	31 (1.3)	5.7 (1.6)	7.8 (1.6)
INT	4	0.92 (1.2)	0.28 (1.4)	1.96 (1.4)	10.8 (1.3)	2.6 (1.5)	3.9 (1.7)
SONT	3	8.0 (1.2)	0.75 (1.2)	1.77 (1.9)	57 (1.1)	13.9 (1.1)	46 (1.7)
Continental means							
EUR	27	4.3 (1.8)	1.08 (1.5)	8.0 (1.9)	49 (1.3)	7.6 (1.6)	11.6 (1.6)
NAMER	21	0.93 (3.5)	0.65 (1.9)	7.1 (3.0)	28 (1.8)	5.6 (1.9)	8.8 (2.4)

The "Boston" (BOS) aerosol was derived from three daily samples at Narragansett when the winds came from the direction of Boston and Providence and SO_2 concentrations were high (July, 20 and Aug. 3 and 6 1982). The New York City (NYC) signature came from six semiweekly samples taken in midtown Manhattan during the 1977–1978 winter. In order to better apply this signature to summer samples elsewhere, we reduced its noncrustal V by 50 percent (K. A. Rahn, D. H. Lowenthal, and N. F. Lewis ["Elemental tracers and source areas of pollution aerosol in Narragansett, Rhode Island." Technical Report, Graduate School of Oceanography, University of Rhode Island (1982)] show that noncrustal V in both New York City and Narragansett decreases from winter to summer by 50 percent relative to other pollution-derived elements.) To better simulate the regional signature near New York, we reduced the Zn, which is abnormally enriched in urban aerosol, by 30 percent (because roughly 30 percent of the Zn is from coarse particles and presumably local, not re-

Vermont, in July 1982, when an unusually strong signal of coal was present and associated with winds from the south-southwest. This singature does not represent pure coal emissions but rather an area where coal emissions are unusually strong. The Canadian smelter (SONT) signal was derived from three samples in southern Ontario roughly 300 km east-southeast of Sudbury (K. A. Rahn, thesis, University of Michigan (1971). It is enriched in As and In. (The small groups of samples defining the signatures were representative distillations of larger sets of data; numbers of samples in each group were kept comparable for statistical purposes).

The samples from Kecskemet and Rorvik allowed us to construct six regional signatures for Europe, three from the East and three from the West. Signature EEURH came from four samples associated with the most prominent mode of As/Se in Kecskemet. Signature EEURS came from three samples at Rorvik during the most intense "black episode" (C. Brosset, Supra) of the past decade.

TABLE 2

Episode of east European aerosol at Sweden and Finland

Dates of Sample (1982)	Sulfate (µg m^{-3})	As/Se	Sb/Se	Noncrustal V/Se	Zn/Se	Noncrustal Mn/Se	In/Se (× 10^3)
Rorvik, Sweden							
11–13 January	2.4	3.0	0.67	15.4	69	13.1	17.4
13–15 January	5.4	9.6	2.4	50	52	26.5	31
15–18 January	12.9	4.0	0.8	5.2	49	6.0	<3
16–20 January*	11.1	7.4	1.85	6.0	70	13.0	16.1
20–21 January*	19.5	8.2	1.68	3.8	65	11.7	12.8
21–22 January*	35.5	6.3	1.68	4.8	63	16.8	16.7
22–25 January	8.3	3.5	1.83	4.2	33	4.5	7.6
25–27 January	3.6	1.8	0.98	14.6	31	3.5	13.1

TABLE 2-continued

Episode of east European aerosol at Sweden and Finland							
Dates of Sample (1982)	Sulfate (μg m⁻³)	As/Se	Sb/Se	Non-crustal V/Se	Zn/Se	Non-crustal Mn/Se	In/Se (× 10³)
			Ahtari, Finland				
17-18 January	6.5	3.4	0.60	9.4	54	3.8	7.2
18-19 January	5.3	2.6	0.64	8.0	66	5.7	11
19-20 January*	3.7	5.5	1.3	8.9	58	9.5	15
20-21 January*	19.4	6.6	1.6	5.7	52	13	13
21-22 January*	9.0	6.8	1.5	7.0	56	11	11
22-23 January*	17.8	5.9	1.6	8.3	52	10	10
23-24 January	0.95	4.6	0.86	10	52	7.6	18

*East European aerosol present

As shown in Table 2, this aerosol was very different from that before and after the episode and had eastern European rather than western European characteristics. These samples made up most of the small upper mode of As/Se at Rorvik shown in FIG. 1. Signature EEURF came from four samples at Ahtari, southern Finland, during the same black episode. Table 2 also shows these samples and how they closely resembled aerosol at Rorvik during the same period. The two signatures of western Europe, WEURS and WEURH, were derived from five samples at Rorvik when the winds were from the southwest and fine samples at Kecskemet when the winds were from the west, respectively. For at least As/Se and noncrustal V/Se, these samples appeared in well-defined modes at the two sites. The last European signature is for Scandinavia (SCANS), as determined from periods of unusually high noncrustal V/Se at Rorvik, which usually coincided with weak circulation or winds from the north.

The western and eastern European signatures confirm the existence of general regional aerosols which appear at various sites in and around large source regions. Because the three eastern signatures are so similar, they can be combined into a general eastern European signature (EEUR), as shown in Table 1. Similarly, the two western European signatures can be combined into the general WEUR. As more data became available from eastern North America, it should be possible to construct general signatures there as well. For illustrative purposes, we have combined the four coastal signatures NE, BOS, NYC, and WASH into ECOAST, which is also shown in Table 1. (All samples from North America and Europe were combined to form the continental signatures NAMER and EUR.) Note that the principal modes of As/Se, noncrustal V/Se, and Zn/Se at Barrow and Bear Island agree quite well with the WEUR and EEUR modes at Rorvik and Kecskemet.

Some of the most significant features emerging from elemental tracers are that the tracing power varies widely from element to element, that most of the tracing power is vested in a very few elements, and that the discriminatory power of an element, as measured by the range of its X/Se ratio and its degree of modality, is similar at widely diverse sites. For example, As/Se and Zn/Se have, respectively, large ranges with well-defined multiple modes and small ranges with single modes at most sites. Thus some elements are inherently much better tracers than others. The reasons for this are probably geochemical. They may be related to large-scale elemental variations in the earth's crust.

TABLE 3

Two estimates of the relative discriminatory power of various elemental ratios on the 48 signature samples of Table 1

	Number of samples misclassified (out of 48)		
Elemental ratio omitted	With 12 individual signatures	With 6 regional signatures	With 2 continental signatures
	1	2	7
As/Se	6	13	13
Sb/Se	1	2	6
Noncrustal V/Se	3	6	7
Zn/Se	2	3	9
Noncrustal Mn/Se	1	4	7
In/Se	2	2	7
As/Se, noncrustal V/Se	13	19	10
Noncrustal Mn/Se, In/Se*	2		
Sb/Se, Zn/Se*		5	
Sb/Se, Zn/Se, noncrustal Mn/Se, In/Se*			8

*Ratios indicated by stepwise discriminant analysis to be lacking in discriminatory power

Table 3 illustrates two ways to measure the relative discriminatory power of tracer elements. In the first, linear discriminant analysis (Linear discriminant analysis is used to define groups from observations with known attributes and then classify other observations into one of these groups (D. F. Morrisson, *Multivariate Statistical Methods* (McGraw Hill, New York, 1976), pp. 230-246). For linear discriminant analysis, we used a program in SAS-79 (SAS Institute, Inc., Cary, NC 1979) on log-transformed data was used to classify the 48 signature samples of Table 1 into the 12, 6 and 2 groups shown in Table 3. Initially, all six of our X/Se ratios were used. Then the samples were reclassified with each of the ratios removed in turn. The greater the discriminatory power of a ratio, the more samples will be misclassified when it is removed. The results showed that As/Se and noncrustal V/Se had the greatest discriminatory power, Zn/Se had somewhat less power, and the other three ratios contributed little or nothing on the average. When both As/Se and noncrustal V/Se were removed, the extent of misclassification became greater than their summed individual effects. As a more sophisticated test of discriminatory power, stepwise discriminant analysis (In stepwise discriminant analysis, variables are added to the discriminant function in the order that they enhance the separation between groups. For stepwise discriminant analysis, we used a program in BMDP, "*Biomedical Computer Programs, P-Series*" (Univ. of California Press, Berkeley, 1979)) was applied to the six ratios (log-transformed) as they were used to segregate the 48 samples into groups of 12, 6, and 2 signatures. The results are shown at the bottom of Table

3. The only two ratios having good tracer power in all three cases were As/Se and noncrustal V/Se.

It may be possible to improve the discriminatory power of our ratios by using discriminant analysis in which elemental ratios are replaced by higher order terms as generated and selected by the group method of data handling (A. G. Ivakhnenko et al, in *Theoretical Systems Ecology*, E. Halfon, Ed. (Academic Press, New York, 1979), p 325) The discriminatory power of optimized functions of ratios seems to be at least 20 to 40 percent greater than that of linear functions. Products

Dust storms, volcanic eruptions, or bursts of aerosol from unexpected point sources of pollution may all provide transient aerosols with unusual signatures which could be understood by use of additional tracer elements.

Once discriminant analysis has been used to determine classification criteria from samples with distinctive signatures, one may classify nonsignature samples into those groups In principle, the origin of an aerosol sample could be determined from its chemical composition alone.

TABLE 4

Classification of nonsignature aerosol samples in North America and Europe

	Classification					
	With 12 Individual Signatures		With 6 Regional Signatures		With 2 Continental Signatures	
	North America	Europe	North America	Europe	North America	Europe
Narragansett. R.I.	98	3	92	9	94	7
Underhill, Vermont	25	10	22	13	29	6
Rorvik, Sweden	21	45	19	47	28	38
Kecskemet. Hungary	0	22	0	22	0	22
	With five regional signatures					
Bear Island. Norway (without In/Se)			1	31		
Barrow. Alaska (without In/Se)			5	28		
	SONT	NE	BOS	NYC	WASH	INT
Narragansett R.I	0	17	17	8	37	22
Underhill Vermont	1	14	1	7	3	9

involving As/Se and noncrustal V/Se are the most useful.

Empirical confirmation that certain elements are crucial to a successful regional tracer system was obtained by comparing our experience in southern Sweden with results of Lannefors et al. H. Lannefors, H. C. Hansson, L. Granat, *Atoms. Environ.* 17, 87 (1983) who took daily aerosol samples for 1 year at Sjoangen. 200 km northeast of Rorvik. Their data, which included S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb but lacked As, Se, Sb, and In, were unable to differentiate between aerosols from eastern and western Europe.

To test whether the criteria on which our seven-element tracer system was based—that the components be pollution-derived, fine-particle, and determined well by neutron activation—are unduly restrictive, we investigated the tracer power of nine other elements (Al, Sc, Cr, Co, Fe, La, Ce, Sm, Th) by means of stepwise discriminant analysis on the same 48 signature samples. These elements are as well determined as the seven basic tracers but are mostly coarse-particle in the aerosol (Cr, Co, and Fe usually have a fine-particle component and La and Ce occasionally do) In general, the tracer power of La, Ce and Sc was comparable to or better than that of Sb, In, and noncrustal Mn but less than that of As, noncrustal V, and Zn. The Al, Sm, and Th appeared to have little promise as tracers, and Fe, Co. and Cr behaved in an intermediate fashion. We do not know how the apparent tracer power of La, Ce and Se is partitioned between their coarse and fine-particle components. The fraction associated with coarse aerosol may be less useful than suggested by these signature samples, because coarse aerosol is not transported as efficiently as fine aerosol Overall, it is probably prudent to measure as many elements as possible (both natural and pollution-derived) in the aerosol, with an eye toward occasions when they could be useful as tracers.

Table 4 shows a geographic classification of unknown samples by our seven-element tracer system. In the upper part of the table, nonsignature samples from Narragansett, Underhill, Rorvik, and Kecskemet have been classified as North American or European based first on 12 individual signatures, then on six regional signatures, and finally on the two continental signatures of Table 1. In general, the posterior probability for membership in one of the source groups was greater than 90 percent. All samples from Kecskemet were classified correctly (as European). At Narragansett. 90 to 95 percent were classified correctly (as North American). At Underhill and Rorvik, however, only 60 to 80 percent were classified correctly. Similar results were obtained when the noncrustal Mn/Se and In/Se ratios were eliminated. Classifying samples by continent is a severe test, however, because it is much more difficult for entire continents than for regions to have distinct signatures.

The center of Table 4 shows how samples at Bear Island and Barrow were classified relative to the five more appropriate regional signatures (SCANS, WEUR, EEUR, ECOAST, INT). Only 1 of 32 (3 percent) and 5 of 33 (15 percent), respectively, were called North American. This confirms our earlier conclusions, reached independently, that Arctic pollution aerosol is strongly Eurasian in origin K. A. Rahn. ibid 15, 1447 (1981); *Idojaras* 86, 1 (1982).

The bottom of Table 4 illustrates how the nonsignature samples at Narragansett and Underhill were classified relative to the six North American signatures At Narragansett, the four coastal signatures accounted for three-quarters of the cases, with the other quarter coming from the interior signature This result confirms with multielemental data the conclusions about domi-

13

nance of coastal aerosol reached earlier from noncrustal Mn and V alone K. A. Rahn, D. H. Lowenthal. and N. F. Lewis ["*Elemental Tracers and source areas of pollution aerosol in Narrangansett, Rhode Island*", Technical Report. Graduate School of Oceanography, University of Rhode Island (1982)] At Underhill, on the other hand, the most common signature is New England (40 percent), followed by other East Coast (30 percent) and the interior (25 percent). Considering Underhill's location in northern New England, this distribution of sources is reasonable.

14

of the As and Se were associated with the interior signal, whereas 60 to 80 percent of the Sb, Zn, In. and noncrustal Mn and more than 90 percent of the noncrustal V came from the coastal sources This type of result is common for Narragansett during summer.

TABLE 7

Least-squares regional coefficients for 14 Narragansett aerosol samples from summer 1979

Sample Dates	SO$_2$ ($\mu g\,m^{-3}$)	Regression Coefficient				
		NE	BOS	NYC	WASH	INT

TABLE 5

Elemental concentrations in five source-area aerosols

Concentration (ng m^{-3})

Element	NE	BOS	NYC	WASH	INT
As	0.060 ± 0.033	0.49 ± 0.15	2.0 ± 0.2	3.2 ± 0.9	1.54 ± 0.40
Sb	0.143 ± 0.048	0.83 ± 0.41	3.1 ± 0.6	2.1 ± 0.7	0.55 ± 0.29
Se	0.37 ± 0.20	1.00 ± 0.60	1.88 ± 0.42	2.4 ± 0.7	1.78 ± 0.79
Noncrustal V	4.0 ± 1.7	35 ± 6	20 ± 4	23 ± 8	34 ± 1.0
Zn	11.1 ± 4.3	37 ± 3	70 ± 17	60 ± 12	18.2 ± 8.0
Noncrustal Mn	2.2 ± 0.3	4.2 ± 0.8	13.0 ± 1.1	9.2 ± 3.4	4.3 ± 2.4
In	0.0028 ± 0.0001	0.0050 ± 0.0040	0.0160 ± 0.0032	0.020 ± 0.006	0.0064 ± 0.0006

TABLE 6

Contributions of various source regions to elements in Narragansett aerosol sample GSO 176, 3 to 8 August 1979

	Weighting Factor	Concentration (ng m^{-3})					
		NE	BOS	WASH	INT	Total predicted	Observed
As	300	0.03	0.06	0.20	0.36	0.65	0.67
Sb	30	0.08	0.10	0.13	0.13	0.44	0.55
Se	100	0.20	0.13	0.15	0.42	0.90	0.90
Noncrustal V	20	2.20	4.42	1.44	0.80	8.9	9.0
Zn	4	6.11	4.68	3.76	4.31	18.9	18.4
Noncrustal	0.4	1.21	0.53	0.58	1.02	3.34	2.00
In	100	0.0015	0.0006	0.00	0.0015	0.0036	0.0040

Discriminant analysis is used to determine which of several signatures is most likely to account for an aerosol sample. In actuality, however, most aerosol samples come from more than one source, either because of the history of the air mass or because of changes in it during sampling. By using least-squares techniques similar to those employed in previous chemical element balance analyses G. E. Gordon, *Environ. Sci. Technol.* 14, 792 (1980), a sample can be apportioned among the various regional aerosols which may have contributed to it (For least-squares apportionments of aerosol we used the program PETMIX, originally developed for petrologic studies [T. L. Wright and P. C. Doherty, *Geol. Soc. Am. Bull.* 81, 1995 (1970)], and a program in SAS-79). For the elemental concentrations of five regional aerosols listed in Table 5 (Tables 5 to 7 are from K. A. Rahn and D. H. Lowenthal, paper presented at the 17th Annual Conference on Trace Substances in Environmental Health. Columbia, Mo., June 13 to 16 1983, published May 1984.), Table 5 shows an apportionment for an August 1979 aerosol sample from Narragansett. In this sample, the abundances of six of the seven tracer elements were accounted for to better than 20 percent by four of the signatures (NYC gave a negative coefficient, so it was eliminated and the regression was rerun with four sources) The weighting factor in Table 6 is really two factors, one to scale the numerical values of the different elements and another, based on Table 3, to weight, As, Se, noncrustal V, and Zn relative to Sb, In, and noncrustal Mn (The final apportionment is insensitive to weighting factor, however.) Note that about half

13-17 July	8.63	0.66	0.11	0.11	0.02	0.07
17-24 July	12.32	0.37	0.26	0.12	0.01	0.20
24-27 July	11.24	0.00	0.36	0.00	0.00	0.56
27-31 July	19.12	0.00	0.19	0.16	0.00	0.47
31 July– 3 August	16.49	0.76	0.00	0.04	0.00	0.34
3-8 August	10.28	0.55	0.13	0.00	0.06	0.24
8-10 August	5.47	0.56	0.08	0.22	0.00	0.23
10-14 August	10.49	0.30	0.37	0.00	0.00	0.19
14-17 August	8.31	1.17	0.07	0.19	0.00	0.00
17-21 August	12.14	0.47	0.35	0.00	0.02	0.00
21-24 August	22.48	0.38	0.47	0.09	0.00	0.00
24-28 August	12.90	0.78	0.17	0.00	0.00	0.16
28-31 August	11.00	0.80	0.05	0.02	0.00	0.14
31 August– 4 September	8.71	0.55	0.16	0.00	0.00	0.27

Table 7 summarizes the apportionments of 14 consecutive semiweekly samples from Narragansett during summer 1979, and shows that the mix of sources can vary strongly in response to large-scale meterology. During summer 1979, Narragansett had two major sulfate episodes, one in July and one in August The first was a "typical" summer episode, with winds from the south to west. The second episode was different, however. It had the highest summer sulfate seen to that time in Narragansett but the lowest (most northeastern) noncrustal Mn/V ratios and the lowest As. Meterological maps showed that this episode was the result of large-scale stagnation in the Northeast of air which had originated largely in the upper Great Lakes and Canada Thus, the first episode appeared to be mid-Atlantic or

interior in origin, whereas the second appeared to be more than from New England and Canada.

The apportionments bore out these observations. The first episode had high regression coefficients from the interior, normal coefficients from Boston, and low coefficients from New England. The second episode, by contrast, had zero coefficients from the interior and normal to high coefficients from Boston and New England. Washington aerosol was negligible throughout the period, contributions from the New York area were low to moderate and irregular.

Although our tracer system is based on primary pollution elements, that is, those emitted directly as aerosol, an important use of the system will be to understand the regional origins of secondary species, such as sulfate and acidity, which are formed in the atmosphere from primary precursors. Sulfate is the most abundant constituent of many remote aerosols, and both sulfate and acidity are of great concern in acid deposition.

Strictly speaking, primary constituents cannot trace secondary constituents. Near strong sources of (primary) aerosol, such as large urban or industrial areas, our tracer system should work poorly for sulfate. Outside such areas, where regional aerosols dominate, a primary tracer system should work better, although there may still be difficulties. In remote areas, primary tracers should work still better because most of the primary precursors, such as SO_2, will have been converted or otherwise removed; that is, the secondary species will have reached quasi-stable proportions. Under these conditions, the aged regional aerosols would effectively contain a sulfate component linked to the primary signature elements.

This appears to be the situation at Underhill, Vt., for example. In a series of 39 daily samples from July and August 1982, we determined the "effective" sulfate in the various regional signatures by first apportioning the seven tracer elements, then regressing the sulfate of each sample against the regional coefficients derived from that sample. The results gave the following approximate concentrations of sulfate: 21 ± 1 g m^{-3} for the interior signature (INT), 7 ± 3 μg m^{-3} for the mid-Atlantic region (WASH), and 3 ± 1 μg m^{-3} for the local aerosol (NE). Based on these values, the predicted sulfate concentrations generally reproduced the observed values to within 25 percent (FIG. 2). This accuracy is comparable to that obtained for the primary tracer elements. In particular, each of the peaks and valleys of sulfate was predicted.

At Narragansett, Rhode Island, however, the same approach gave poorer results. FIG. 2 shows the observed and predicted sulfate for 21 semiweekly samples during June to September 1979. The fractional errors were twice as large as at Underhill, neither peaks or valleys were predicted correctly, and a period of low sulfate at the beginning was missed entirely. This behavior is consistent with Narragansett's less remote location and with the abundant SO_2 observed there even during summer (2 to 20 g m^{-3}) (T. R. Fogg, personal communication). The "noise" in sulfate at Narragansett most likely results from variable and unpredictable oxidation of this subregional SO_2, on a scale too small to be seen at Underhill. Time traces of the elements at Narragansett are considerably more irregular relative to each other and to sulfate than at Underhill. Thus, it appears that both primary and secondary aerosol of the coastal Northeast are more local in origin than those in interior New England and that control of this aerosol

and its deposition will require different strategies for different parts of the Northeast.

We claim.

1. A method to determine regional sources of pollution aerosol which includes.
   (a) selecting empirically a small number of suitable tracer elements which are pollution-derived, associated with submicron-sized particles, and accurately analyzable in the aerosol.
   (b) measuring the concentrations of each tracer element in multiple samples of regionally-representative aerosol at multiple sites in each source region whose signature is to be determined,
   (c) expressing the measured results as ratios to one of the tracer elements;
   (d) defining the elemental signature of the source region as the collection of elemental ratios and associated standard deviations which best represents that region's aerosol;
   (e) determining the source region's signature from modes in the logarithmic frequency distributions of the elemental ratios of samples taken in source region;
   (f) measuring the concentrations of each tracer element in multiple samples of an aerosol from a receptor region;
   (g) comparing the elemental ratios from the receptor region to the signatures from possible source regions to determine the most probable source region.

2. The method of claim 1 wherein the tracer elements are selected from the group consisting essentially of As, Sb, Se, Zn, In, noncrustal Mn, noncrustal V, Pb, Cd, Ag, C, and combinations thereof.

3. The method of claim 1 wherein the common denominator of the elemental ratios is selected from the group consisting essentially of Se, Zn, Pb, and C.

4. The method of claim 1 which includes:
   checking the stability during transport of a regional signature determined solely within a region by measurements outside the region.

5. The method of claim 1 which includes:
   identifying the perturbing effects of a local source by performing factor analysis on the raw data from a given site;
   isolating the local source on its own factor;
   determining the composition of the source from that factor; and
   eliminating the perturbing effects of that source by considering it as a separate signature subsequently.

6. The method of claim 1 which includes:
   determining the most probable area of origin of unknown samples by discriminant analysis of elemental ratios.

7. The method of claim 1 which includes:
   apportioning aerosol samples of mixed origin into regional contributions by least-squares fitting of the signatures (element by element) to the sample.

8. The method of claim 1 which includes
   apportioning secondary constituents such as sulfate or other primary constituents such as elemental carbon, in a series of ratios at a single site, into regional contributions by regressing their concentrations against the regional coefficients of the samples.

9. A method to determine regional sources of pollution aerosol which includes

4,603,575

17

(a) selecting empirically a small number of suitable tracer elements which are pollution-derived, associated with submicron-sized particles, and accurately analyzable in the aerosol;

(b) measuring the concentrations of each tracer element in multiple samples of regionally-representative aerosol at multiple sites in each source region whose signature is to be determined;

(c) expressing the measured results as ratios to one of the tracer elements;

(d) defining the elemental signature of the source region as the collection of elemental ratios and

18

associated standard deviations which best represents that region's aerosol;

(e) determining the source region's signature from the characteristics of samples taken during periods of atmospheric stagnation;

(f) measuring the concentrations of each tracer element in multiple samples of an aerosol from a receptor region;

(g) comparing the elemental ratios from the receptor region to the signatures from possible source regions to determine the most probable source region.

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151